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Communication

A dual-mode microwave resonator for double electron–electron spin resonance spectroscopy at W-band microwave frequencies

Igor Tkach [a,*], Giuseppe Sicoli [a], Claudia Höbartner [b], Marina Bennati [a,*]

[a] Max Planck Institute for Biophysical Chemistry, Research Group Electron Paramagnetic Resonance, Am Faßberg 11, 37077 Göttingen, Germany
[b] Max Planck Institute for Biophysical Chemistry, Research Group Nucleic Acid Chemistry, Am Faßberg 11, 37077 Göttingen, Germany

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ABSTRACT

We present a dual-mode resonator operating at/near 94 GHz (W-band) microwave frequencies and supporting two microwave modes with the same field polarization at the sample position. Numerical analysis shows that the frequencies of both modes as well as their frequency separation can be tuned in a broad range up to GHz. The resonator was constructed to perform pulsed ELDOR experiments with a variable separation of "pump" and "detection" frequencies up to $\Delta\nu$ = 350 MHz. To examine its performance, test ESE/PELDOR experiments were performed on a representative biradical system.

1. Introduction

Modern EPR spectroscopy relies on a repertoire of different continuous-wave (CW) and pulsed techniques. Among the most important is the pulsed electron–electron double resonance technique (PELDOR, also called DEER), which allows measurement of long range distances (2–8 nm) between two paramagnetic species in macromolecules [1–6]. At high magnetic fields, PELDOR experiments can also deliver information about the relative orientations of paramagnetic species [7–13]. This is a valuable information to study conformational changes of macromolecules or assemblies of protein complexes in which paramagnetic centers are rigidly embedded. This offers the possibility to reconstruct a biradical structure when a crystal structure is not available.

Since two microwave frequencies are required to perform PELDOR, the bandwidth of an EPR resonator is a crucial issue for the experiment. Typically, one of the frequencies is set to the center of the resonator dip and the second frequency is placed on the side of the dip, where the efficiency of a microwave excitation field is strongly reduced. On commercial and single mode W-band resonators the frequency difference for efficient PELDOR measurements can be set only in the range of $\Delta\nu$ = 20–60 MHz [11,14], which is not sufficient to cover all orientations resolved at high fields. In many cases, to do this one has to separate the "pump" and "detection" frequencies up to $\Delta\nu$ = 200–350 MHz and more. With a single mode resonator, particularly at frequencies above 90 GHz, this still represents a challenge. Our attempts to employ a commercial low-Q cylindrical resonator with $\Delta\nu$ up to 150 MHz revealed a considerable decrease in signal sensitivity [15]. On the other hand, PELDOR experiments without the use of any resonator are feasible only if very large microwave powers (1 kW) are available [13].

Thus, we propose that the solution is provided by a dual-mode resonator, in which the frequency separation can be set to "pump" and "observe" the non-collinear radicals in a pair. Dual-mode microwave resonators are already known in EPR spectroscopy [6,16–19]. However, these resonators were adapted for X-band frequencies only (e.g. about 9 GHz) and have never been used for orientation selective PELDOR. The resonance frequencies of the modes are usually fixed (except for the designs in Refs. [6,17], where the frequencies could be tuned) and their polarizations are perpendicular to each other [6,16,17]. Furthermore, excitation of allowed transitions, like in a PELDOR experiment, requires orthogonality of both modes to the static magnetic field B_0. The resonance configurations with the nearly collinear polarizations of the modes, which were presented in Refs. [18,19] using dielectric rings, cannot be used at high frequencies due to the miniature dimensions of the dielectric inserts. An application of a multimode Fabry–Pérot resonator in combination with a W-band high-power system was reported in Ref. [20].

In this paper we present a dual-mode resonator, in which both microwave modes have the same polarization and the

* Corresponding authors. Fax: +49 (0)551 201 1383.
E-mail addresses: Igor.Tkach@mpibpc.mpg.de (I. Tkach), Marina.Bennati@mpibpc.mpg.de (M. Bennati).

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effective B_1-field profile over the sample. Furthermore, the frequency difference between the modes can be tuned in a broad range during an experiment. The cavity differs from the others mentioned above and allows performing PELDOR experiments at W-band with a variable separation of "pump" and "detection" frequencies up to 350 MHz [21]. Its numerical analysis as well as construction and test results are discussed.

2. Cavity design and principle of performance

The general design of the resonator is presented in Fig. 1. It consists of two cylindrical hollow portions axially connected to each other and separated by a coupling junction (see Fig. 1, inset), which consists of: (1) a lossless dielectrical window (mica), (2) a thin conducting plate (sheet of a copper foil), and (3) two lateral conducting (gold coated brass) slabs.

The conducting plate is placed in the plane perpendicular to the longitudinal axis of the resonator. It covers the dielectrical window and forms a disk-shaped surface between the resonator portions. In radial direction, the conducting plate is surrounded by a spacing. Such a configuration forms a resonance structure being able to support standing waves of microwave modes essential for the EPR experiment, i.e. TE_{011} and TE_{012} with the magnetic field maximum on the longitudinal axis (details below).

The diameter of the hollow portions is equal to 4.16 mm. There are two pistons, each at the end of each portion, which face each other and can be moved symmetrically along the longitudinal axis of the resonator inside the hollow portions. The pistons delineate the top and the bottom of the joint compartment formed by the hollow portions. The distance between the pistons can be changed from 3 to 20 mm by a fine tuning mechanism. This function is implemented for two reasons: (1) to adjust the frequencies of both modes and (2) to tune the mutual position of the pistons with respect to the coupling junction in order to adjust the condition for a dual-mode excitation.

One of the pistons, which shorts the upper resonance portion, contains an opening to introduce a paramagnetic sample into the resonator. The sample tube with a liquid or solid specimen can be guided into the upper resonance portion with a suited sample holder. In order to avoid the degradation of the dual-mode configuration while inserting the sample, the tuning of both portions was designed to be independent to compensate for the change of the resonance conditions in the upper section.

The coupling with the WR10 rectangular waveguide, which connects the resonator to the microwave source, is performed via a small iris on the back side of the upper section. It is located at the point, where the microwave magnetic field strength of both modes has the same orientation as the magnetic field of a dominant mode (TE_{10}) in the waveguide. The diameter of the coupling iris equals to 0.9 mm. To avoid undesirable losses of the microwave power, the thickness of the wall around the iris has been minimized (~0.1 mm). All parts of the resonator, except the coupling junction, were made of brass. Gold coating was applied afterwards.

The main advantage of the cylindrical configuration is that for the TE_{011} mode there are no currents flowing between the cylindrical part of the resonator and the plungers used to short the ends of the cavity. This means that the diameter of the backshorts is not critical to the operation and Q of the cavity. In principle, to support the TE_{011} mode, it is sufficient to use a plunger of a smaller diameter, or even a thin plate. Circular microwave currents will be induced in the plate, therefore it will play a role of a "semi"-short. Of course, the boundary conditions, and therefore the resonance frequency, of such a resonance structure will differ from those of a resonator with standard shorts (extended thickness and the diameter approaching the diameter of the resonator).

If we place such a plate in the middle of the cylinder, two resonance portions with equal dimensions will be formed. Therefore, the TE_{011} mode will be supported in both portions. These modes will oscillate in phase with the same resonance frequency. Such configuration supports also another mode of cylindrical geometry, i.e. the TE_{012} mode (half-wavelength variations oscillate with the π-phase shift in the resonance sections). This mode exhibits a higher resonance frequency determined by the mode indices and the total dimensions of the resonator (first and the second resonance sections), as described in Ref. [22].

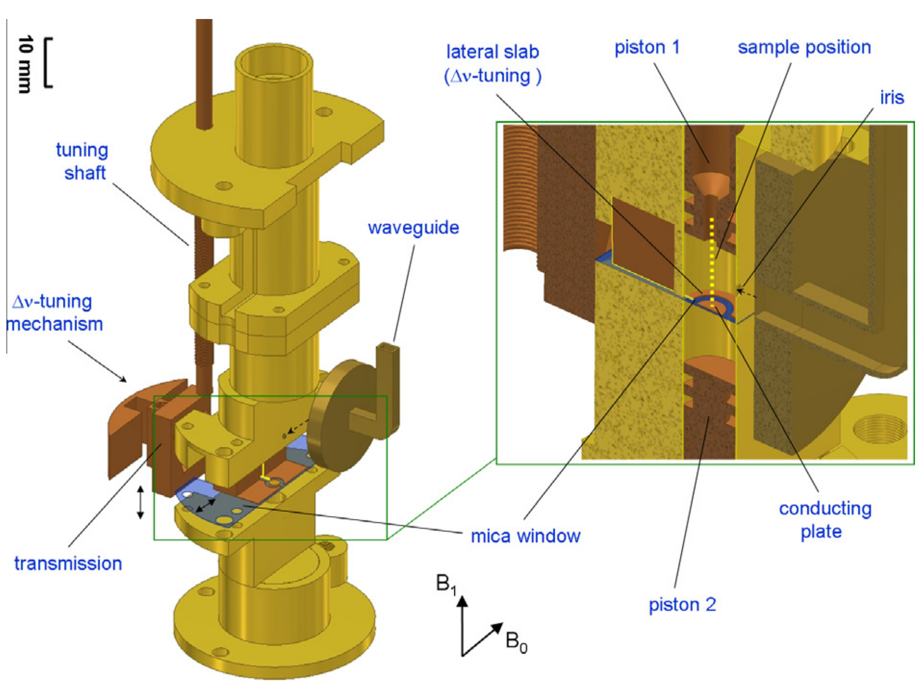

Fig. 1. General and cross-sectional view of the dual-mode resonator.

Since in both cases we deal with cylindrical modes, the field configuration of the standing wave in the single portions is the same and the sample can be kept at the axial position of the single resonator section during the experiments. This is significant because in a PELDOR experiment the effective B_1-field profile over the sample is desired to be the same for both modes, thus the modes should have the same field polarization. Furthermore, such a resonator can be easily constructed in a configuration, in which B_1 is perpendicular to the external field of a superconductive magnet, for instance of the commercial Bruker W-band ESR spectrometer (ElexSys 680).

3. Numerical simulations

The proposed resonance structure was analyzed with the CST Microwave Studio® software (CST – Computer Simulation Technology AG, Darmstadt, Germany). The electromagnetic field distributions, eigenfrequencies and scattering parameters (S_{11} and S_{12}) were calculated as a function of the distance between the plungers, the size of the conducting plate, and the position and the shape of the lateral tuning slabs. The primary goal of the simulations was to optimize the geometry of the cavity and find a proper way to tune the frequencies, particularly the frequency separation between the modes. Fig. 2a shows schematically the magnetic field distribution of the TE_{012} mode appearing at higher resonance frequencies. The standing wave pattern of the TE_{011} modes (oscillating in the phase in both resonance portions) is shown in Fig. 2b.

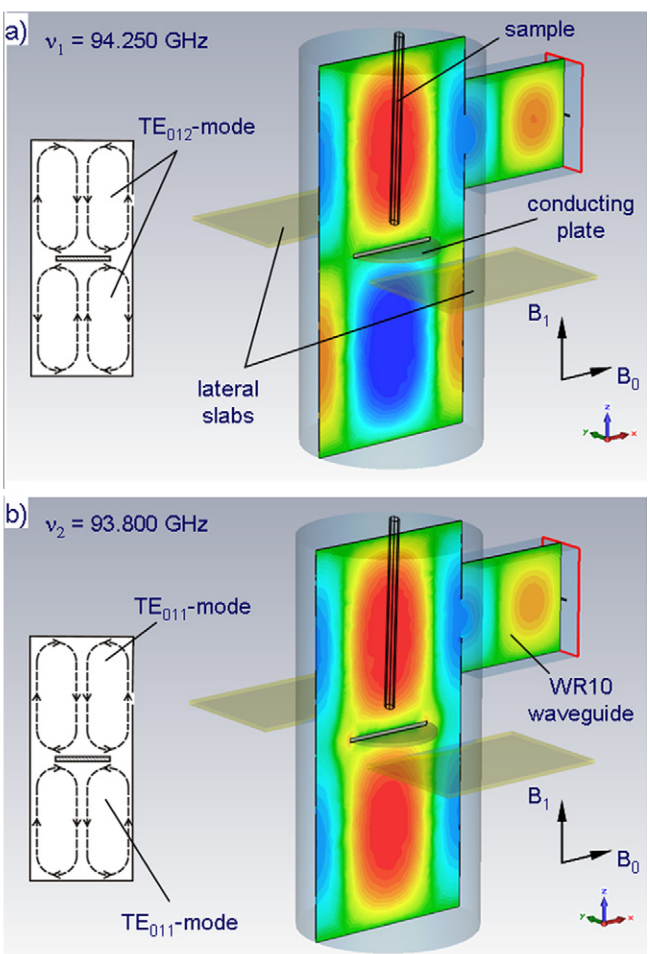

Fig. 2. Simulated magnetic field distribution of the (a) TE_{012} mode and (b) TE_{011} modes in the dual-mode resonance structure. The B_1 magnitude in the XZ-plane cross-section is shown. Dark-red and dark-blue colors correspond to the oscillations shifted in the phase by π.

The numerical analysis shows that in order to support the two modes at the sample, it is essential to have the conducting plate arranged at a precise location on the longitudinal axis: this is in the middle of the resonance compartment between the half-wavelength variations of the standing wave pattern of the TE_{012} mode, i.e. in the minimum of its magnetic and electric field strength (i.e. a node). A slight deviation (up to 0.2 mm) is acceptable, however it leads to a partial degradation of the dual-mode configuration. Larger deviations cause a complete degradation of the TE_{012} mode.

It was found that the frequency of the TE_{011} microwave mode depends on the thickness of the conducting plate and the radial width of the spacing around the plate. By changing the size of the conducting plate, the frequency of the TE_{011} mode can be adjusted relative to the frequency of the TE_{012} mode (see Fig. 3a), while the configuration (mode type) is retained. Furthermore, the calculated Q-factors of the modes vary only in the range of up to 20% with the change of the plate size. Thus, the initial frequency of the TE_{011} mode can be set very effectively by selecting a plate with a predetermined diameter and thickness. Subsequently, it is possible to reduce the frequency difference of the modes by inserting the lateral metallic slabs into the resonator. In this way the frequency of the lower mode (TE_{011}) will be shifted to upper values, while the frequency of the TE_{012} mode will be almost unaffected (Fig. 3b). This is due to different boundary conditions for both modes. With the change of the lateral position of the slabs (as well as with the change of the plate size) the boundary conditions for the TE_{011} mode will be modified, while for the TE_{012} these are kept unchanged. To avoid the degradation of the TE_{012} mode and diminish the tuning effect for it caused by its perturbation, the slabs must be inserted at the same axial position where the conducting plate is placed.

This principle has been used to design a tuning mechanism that changes the frequency difference $\Delta\nu$ during the PELDOR experiment. The laterally movable conducting slabs (~0.1 mm thickness) together with the conducting plate form a slit-shaped spacing (diaphragm) through which the first and second resonance sections are coupled (see Fig. 1 inset). The tuning slabs can be synchronously moved in opposite directions thus changing the slit-shaped spacing around the plate. Movement of the slabs is guided in the thin nook (0.1 mm), which is formed in the upper section. The change of the spacing leads to a shift of the resonance frequency primarily of the TE_{011} mode, and thus, to the desired change of the frequency separation.

The frequencies of the microwave modes can be also adjusted by converse movement of the pistons. With their adjustment, the longitudinal length of the resonator can be varied resulting in a certain frequency of each mode. Thus, the microwave modes can be tuned with nearly the same frequency separation by synchronous movement of the pistons symmetrically with respect to the axial position of the conducting plate. It is of particular importance to adjust the pistons in a manner to keep the assembly resonant for the TE_{012} mode, i.e. the resonance portions must be "symmetrical" with respect to the half-wavelength variations of the standing wave pattern of this mode. This feature is critical at high (W-band) frequencies, where the miniature geometry of a microwave resonator is very sensitive to small changes in experimental conditions.

4. Test results

The dual-mode resonator was incorporated into a probe head that fits in the liquid He cryostat of a commercial Bruker W-band (94 GHz) ESR spectrometer (ElexSys 680) to perform low

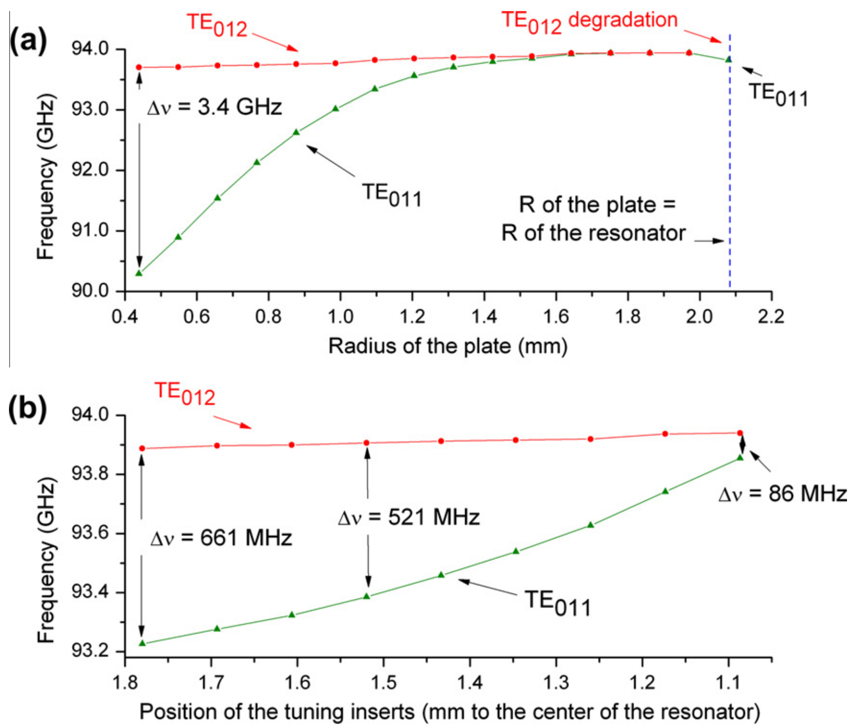

Fig. 3. (a) Simulated variation of the frequencies of the TE_{011} and TE_{012} modes vs. radius of the conducting plate separating the resonance portions. Simulation parameters: "Frequency domain solver", material – gold, thickness of the plate = 0.1 mm, longitudinal length of the resonance portions = 4.53 mm, dielectrical window not included. (b) Simulated variation of the frequencies of the TE_{011} and TE_{012} modes vs. position of the conducting inserts. Simulation parameters: "Frequency domain solver", material – gold, radius of the plate = 1.1 mm; thickness of the plate = 0.1 mm, length of the resonance portions = 4.53 mm, dielectrical window not included.

temperature experiments (down to liquid He). It has been tested on different model samples at room and at low temperatures.

Both modes could be excited during the experiments (see Fig. 4a and b) while the frequency separation has been varied in the range from 70 to 350 MHz. The maximal frequency separation of the resonator was initially set close to 350 MHz by choosing a plate size of 1.25 mm radius and 0.1 mm thickness. The thickness of the mica window was approximately 0.2 mm. A larger frequency separation should be possible with the smaller radius of the plate (see Fig. 3a). However, practically, the tuning of the resonator was limited by the width of the frequency sweeper (~350 MHz).

The observed *Q*-factors of the unloaded cavity for both modes were about 4400 and 2900 for $TE_{012}(\nu_1)$ and $TE_{011}(\nu_2)$, respectively. To determine the B_1 microwave field strengths produced by both modes the echo-detected transient nutation of the electron spins was recorded [23]. The magnetic field B_1, oscillating at the electron spin Larmor frequency, forces the resonant spins to nutate at the angular frequency $\varpi = \gamma_e B_1$, where γ_e is a gyromagnetic ratio of the unpaired electron. The nutation experiments were performed at room temperature on a standard BDPA (α,γ-bisdiphenylene-β-phenylallyl) radical sample with an available microwave power of ~400 mW at the output of the bridge. The nutation curves are displayed in Fig. 4c and yielded frequency values of 8.6 MHz and 8.1 MHz, corresponding to $B_1 \approx 3.1$ G and $B_1 \approx 2.9$ G for the $TE_{012}(\nu_1)$ and $TE_{011}(\nu_2)$ modes, respectively. Such field strengths allowed detection of the spin echo in both dips with $\pi/2$ pulses varying in the range of 28–50 ns. The variation in pulse lengths was caused by different sample-to-sample properties and by the cavity specifications at different stages of its development. The behavior of the modes, i.e. their response to the plunger adjustments and $\Delta\nu$-tuning was consistent with the predictions from the numerical analysis.

The four-pulse PELDOR sequence [11] was applied in all PELDOR experiments. The π pulses used for both detection and pumping were in the range of 56–100 ns corresponding to a range of excitation bandwidths approximately of 18–10 MHz. As an example, Fig. 5b demonstrates the PELDOR trace recorded on a RNA duplex specifically labelled with two nitroxide (TEMPO) radicals at cytosines at positions 3 and 13 of the duplex. The labelled RNA was dissolved in the water/glycerol (40%) mixture at concentration 60 μM (120 μM spin concentration). The effective volume of the sample was approximately 1 μL. Above, in Fig. 5a, the electron spin echo-detected ESR spectra of the TEMPO labels mesured in different resonator dips (ν_1 and ν_2) are presented. Both the ESE spectra and the PELDOR trace were recorded at 40 K. The S/N ratio of the ESE spectra was about a factor of three less in comparison with the spectra obtained under identical conditions with a commercial single mode cylindrical resonator (Bruker EN600-1021H). After optimization of power losses in the waveguide between the cavity and a detector, the sensitivity of the detection system with the dual-mode cavity could reach approximately the same value as with the standard Bruker commercial high-Q resonator. However, in contrast to the single mode resonator, the S/N ratio obtained with the dual-mode resonator is independent on the microwave frequency separation necessary for PELDOR experiments. Furthermore, the same measurements carried out in X-band with the use of a Bruker dielectrical cavity (EN4118X-MD-5) and the sample volume scaled to X-band dimensions (~65 μL) deliver ESE spectra with the S/N ratio approximately 3.5 times less in comparison with the dual-mode cavity.

As it is shown in Fig. 5a, the pumping pulse for the PELDOR experiment was set in the g_x spectral region and the observer sequence at g_z with the frequency separation of 191 MHz to probe the orthogonal orientations of the spin bearing molecules in a pair. The W-band PELDOR data is consistent with previous experiments performed at X-band, which indicated a perpendicular component of the dipolar tensor of 1.6 MHz, i.e. a distance of 3.2 nm [24]. The Pake pattern, however, (Fig. 5c) obtained from the trace measured at W-band shows a lack of the $2\nu_{dd}$, which is due to orientation selectivity at high fields.

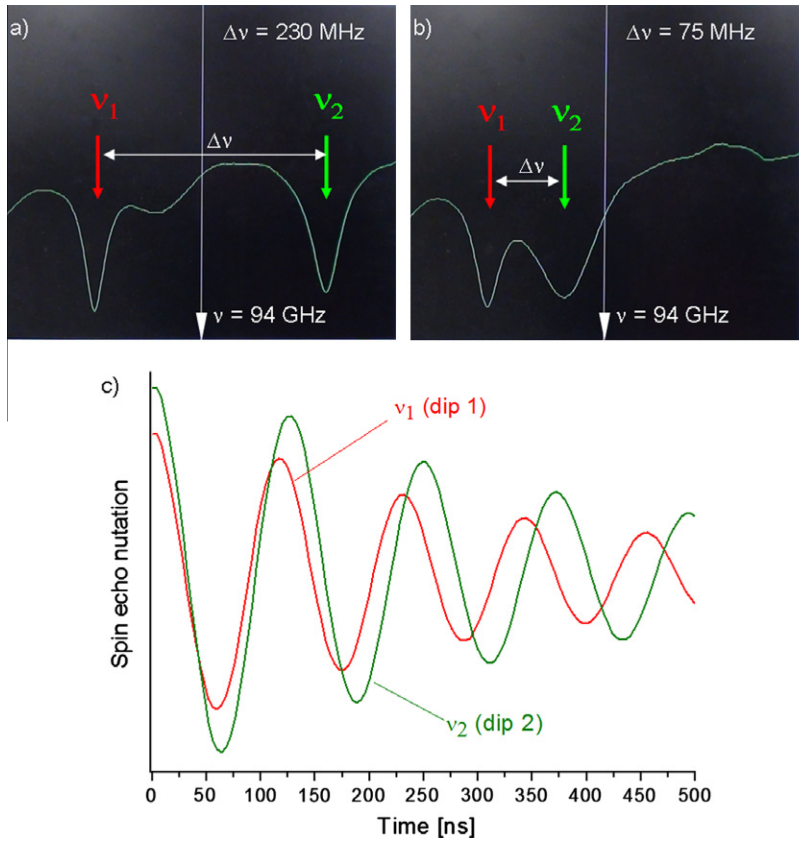

Fig. 4. Tuning curves of the dual-mode resonator at different frequency separation between the modes: (a) $\Delta\nu$ = 230 MHz, (b) $\Delta\nu$ = 75 MHz; (c) typical transient nutation curves measured with the detection of the ESE modulation of the BDPA radical standard sample in different resonator dips at 400 mW maximum output power of the microwave bridge. The frequency separation was set to 200 MHZ.

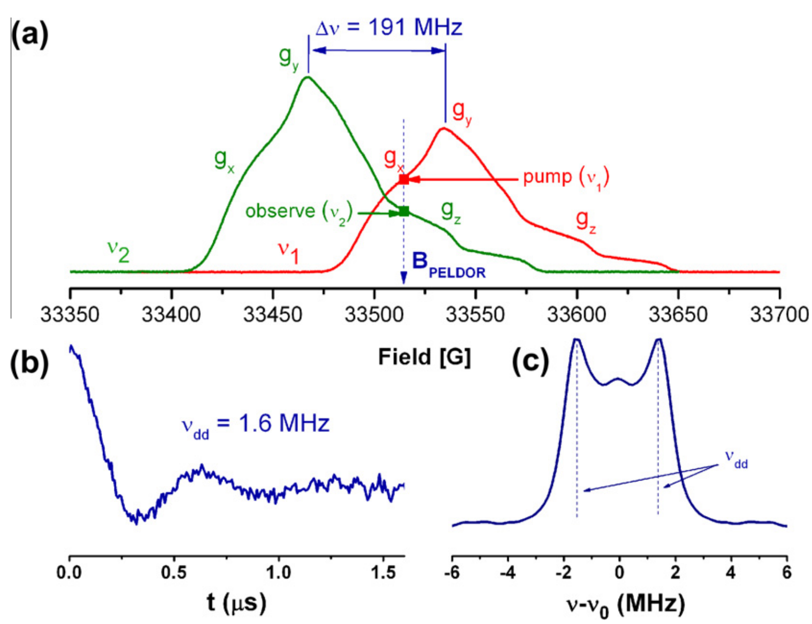

Fig. 5. (a) ESE spectra measured on a labelled RNA at 40 K with the different microwave frequencies corresponding to the resonance frequencies of both modes and (b) PELDOR trace recorded on the sample. PELDOR experiment was performed with the $\Delta\nu$ of 191 MHz between the "pump" and "detection" frequencies at the following experimental conditions: T = 40 K, ν_{pump} = 93.889 GHz, $\nu_{detection}$ = 93,698 GHz, $t(\pi)_{pump}$ = 100 ns, $t(\pi)_{detection}$ = 96 ns, τ_1 = 350 ns, τ_2 = 2400 ns, 3800 scans have been accumulated for 16 h at pulse repetition rate 0.2 kHz. (c) Fourier transformation (Pake Pattern) of the PELDOR trace.

5. Summary

We have demonstrated that a dual-mode resonator can be constructed and employed for ESE and PELDOR experiments at 95 GHz. It has the following advantages and features: (1) it supports two microwave modes with the same polarization at the sample position (B_1-s are collinear); (2) it allows performing PELDOR experiments with a larger (up to 350 MHz) separation between pump and detection frequencies; (3) a paramagnetic sample can be placed at the location of the maximum magnetic field strength of both modes and the effective volume B_1-field profile over the sample is nearly the same at both frequencies; (4) the microwave fields of both modes are sufficiently strong to produce reasonably short microwave pulses ($\pi/2$ >= 28 ns) with the power available in commercial spectrometers.

Even at the early stage of the development, the presented resonator is a "user-friendly" device. The cavity has a cylindrical configuration, which is very convenient for EPR, particularly in W-band. It is tunable and the tuning procedure is similar to the tuning of the standard cylindrical resonator. Its design allows a quick replacement of a paramagnetic sample during an experiment. The cavity is expected to be even more attractive after a number of improvements, which are important for the cavity specifications, however, are not principal for a basic operation.

Our work is going on towards the further improvements, since, to our opinion, the dual-mode cavity has a high potential for applications. It represents an alternative to the high power nonresonant-probehead systems in the case, when the high power sources/spectrometers are not available or they are not applicable because of sample properties (amount of the sample, severe dielectrical losses and a possible damage because of heating), thus extending the abilities of the W-band dual-frequency spectroscopy.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmr.2011.01.012.

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