Journal of Magnetic Resonance 214 (2012) 237–243

Contents lists available at SciVerse ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

A tunable general purpose Q-band resonator for CW and pulse EPR/ENDOR experiments with large sample access and optical excitation

Edward Reijerse [a,*], Friedhelm Lendzian [b], Roger Isaacson [c], Wolfgang Lubitz [a,*]

[a] Max-Planck-Institut für Bioanorganische Chemie, 45470 Mülheim an der Ruhr, Stiftstr. 34-36, Germany
[b] Max-Volmer-Laboratorium, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany
[c] Department of Physics, University of California, San Diego, 9500 Gilman Dr., La Jolla, CA 92093, USA

ARTICLE INFO

Article history:
Received 29 July 2011
Revised 11 November 2011
Available online 30 November 2011

Keywords:
Microwave resonator
Q-band
Pulse EPR
ENDOR
ELDOR

ABSTRACT

We describe a frequency tunable Q-band cavity (34 GHz) designed for CW and pulse Electron Paramagnetic Resonance (EPR) as well as Electron Nuclear Double Resonance (ENDOR) and Electron Electron Double Resonance (ELDOR) experiments. The TE_{011} cylindrical resonator is machined either from brass or from graphite (which is subsequently gold plated), to improve the penetration of the 100 kHz field modulation signal. The (self-supporting) ENDOR coil consists of four 0.8 mm silver posts at 2.67 mm distance from the cavity center axis, penetrating through the plunger heads. It is very robust and immune to mechanical vibrations. The coil is electrically shielded to enable CW ENDOR experiments with high RF power (500 W). The top plunger of the cavity is movable and allows a frequency tuning of ±2 GHz. In our setup the standard operation frequency is 34.0 GHz. The microwaves are coupled into the resonator through an iris in the cylinder wall and matching is accomplished by a sliding short in the coupling waveguide. Optical excitation of the sample is enabled through slits in the cavity wall (transmission ~60%). The resonator accepts 3 mm o.d. sample tubes. This leads to a favorable sensitivity especially for pulse EPR experiments of low concentration biological samples. The probehead dimensions are compatible with that of Bruker flexline Q-band resonators and it fits perfectly into an Oxford CF935 Helium flow cryostat (4–300 K). It is demonstrated that, due to the relatively large active sample volume (20–30 μl), the described resonator has superior concentration sensitivity as compared to commercial pulse Q-band resonators. The quality factor (Q_L) of the resonator can be varied between 2600 (critical coupling) and 1300 (over-coupling). The shortest achieved $\pi/2$-pulse durations are 20 ns using a 3 W microwave amplifier. ENDOR (RF) π-pulses of 20 μs (^{1}H @ 51 MHz) were obtained for a 300 W amplifier and 7 μs using a 2500 W amplifier. Selected applications of the resonator are presented.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is an important analytical tool in a variety of different research fields from chemistry, physics, and materials science to biological and medical research. An essential part of the EPR spectrometer is the microwave resonator, which accommodates the sample to be investigated and which determines the critical experimental parameters such as the sensitivity and time resolution.

For the most common EPR frequency band (X-band, ca. 9.5 GHz) a large variety of dedicated commercial microwave resonators are available [1], which have been optimized for different purposes like maximum sensitivity, small sample size, or highest time resolution (largest bandwidth).

Resonators which are designed to operate at X-band (9 GHz) frequencies are usually of a type which does not allow frequency tuning. For CW EPR the rectangular TE_{102} cavity serves as standard since it combines a reasonable filling factor with a relatively high quality factor (Q). In addition, it is not very susceptible to samples with dielectric losses. Also it can be easily combined with a cold finger cryostat which greatly simplifies sample loading. For specific applications like pulse EPR and (pulse) Electron Nuclear Double Resonance (ENDOR) the convenient TE_{102} cavity design usually has be abandoned due to the additional requirements of large bandwidth and the need to accommodate an RF coil. For these applications dedicated resonators have been developed [2–9]. Since X-band sources (Gunn oscillators and Klystrons) are usually tunable over a relatively wide range the need for cavity tunability is not very high.

For many applications, in particular for biological systems, a multi-frequency approach is required in order to unravel complex spectra. This includes EPR experiments at Q-band (35 GHz), W-band (94 GHz) and even higher frequencies (120, 240 up to

* Corresponding authors.
E-mail addresses: reijerse@mpi-muelheim.mpg.de (E. Reijerse), wolfgang.lubitz@mpi-mail.mpg.de (W. Lubitz).

1090-7807/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jmr.2011.11.011

275 GHz). At Q-band frequencies (35 GHz) the cylindrical TE_{011} cavity is the most frequently used resonator for multiple applications including pulse EPR and ENDOR [1]. This is because the relatively large size of the cavity body makes it easier to machine than scaled down versions of e.g. a TE_{102} cavity. Also it is quite straight forward to vary the resonance frequency by moving one or both plungers in and out. This is an important feature since at 35 GHz the usual microwave sources (Gunn oscillators) are not tunable over a wide range while in contrast the frequency shifts of the resonator upon inserting the sample can be appreciable. To combine a tunable TE_{011} cylindrical resonator with field modulation, rf coils (ENDOR) and optical excitation capabilities is quite challenging. Only a few groups have reported attempts in this direction. Already in the 70ties the group of Feher and Isaacson used a Q-band ENDOR resonator optimized for CW-ENDOR [Isaacson and Feher, private communication]. Also the Hoffman group [10] have successfully utilized a CW/pulse ENDOR Q-band resonator. Sienkiewicz et al. [11] described the first tunable Q-band ENDOR resonator. The groups of Schweiger and Jeschke have developed several specialized Q-band resonators e.g. for CW and pulse EPR [12], large microwave excitation pulse EPR and CW EPR [13] as well as large sample access pulse EPR and ENDOR [14]. Recently, also a tunable Q-band resonator was described optimized for ESE-ENDOR [15].

Our group specializes in pulse EPR and ENDOR at X- and Q-band on metalloproteins and radical proteins including photo excited systems [16–20]. Especially for Q-band pulse ENDOR measurements a cavity with a good filling factor and high ENDOR efficiency is required. The original Bruker ER 5106 QT low temperature Q-band resonator with ENDOR option did not fulfill these requirements as it was originally designed for CW EPR/ENDOR. Its successor, the dielectric model EN5107 is very efficient in microwave and RF power conversion but, at the same time, has a limited sample access (1.6 mm diameter). Since we required a CW/pulse ENDOR resonator compatible in sample access to the standard CW Q-band resonator (3 mm) we decided to develop and built a general purpose Q-band CW/pulse EPR/ENDOR resonator allowing optical access and large sample sizes. As will be shown, our improved resonator has several features which are particularly useful for pulse EPR/ENDOR on metalloproteins and (bio)radicals. The internal 2 turn ENDOR coil is extremely robust and can be used in CW ENDOR up to 500 W and in Pulse ENDOR up to 2.5 kW rf power. In addition, the resonator has good CW EPR properties (1 mT modulation at 100 kHz) and a generous light access (3 mm spot, ~60% transmission). The 3 mm sample tube access affords high sensitivity for biological samples at low concentrations. The same sample tubes can be used with high sensitivity also for 9.5 GHz standard frequency EPR spectrometers. This allows measuring one and the same sample tube at 9.5 GHz and at 34 GHz EPR, which is often an important requirement for investigating biological systems.[1]

2. Technical description

The cavity body used in pulse EPR/ENDOR experiments was constructed as a cylinder (0.5 mm wall thickness) of 11.0 mm inner diameter from iron free brass. The height of the cylindrical cavity on resonance (34 GHz) is 9.0 mm (determined with a Wilmad high precision 3 mm o.d. (2.0 mm i.d.) quartz sample tube inserted). This ensures a high conversion of incident microwave power to microwave field amplitude inside the cavity. The modular design of the resonator allows easy exchange of different resonator bodies (Fig. 1a, see below). For pulse EPR experiments it is important to obtain a resonance bandwidth of more than 20 MHz. Therefore the brass cylinder was not gold coated and the Iris for coupling

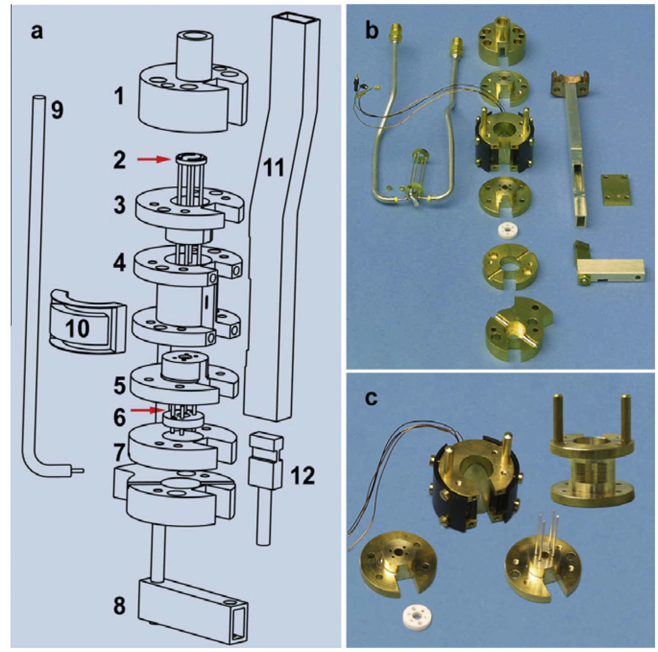

Fig. 1. (a) Exploded view of the Q-band TE_{011} ENDOR resonator probehead; (1) Upper cover; (2) ENDOR posts; (3) upper (movable) plunger; (4) resonator body with iris on the right (flattened) side; (5) lower (fixed) plunger; (6) RF contact plate; (7) coax clamps; (8) drive bar for sliding short; (9) RF coax line; (10) modulation coil body; (11) coupling wave guide; (12) sliding short. (b) Photo of the disassembled resonator showing the parts in panel (a). The input and output coax lines are connected to the ENDOR coil and the modulation coils are mounted to the resonator body. (c) Photo of the resonator body with modulation coil attached (using the black caps). The upper and lower plunger, detailing also the silver posts making up the RF coil as well as the MACOR contact plate (white). In addition a "naked" resonator body with slits (12 cuts of 0.3 mm, 0.5 mm apart giving a 3 mm wide 60% optical access) is shown.

the microwave from the waveguide into the cavity was slightly enlarged (2.5 × 0.5 mm slot, see Fig. 1, part ⟨4⟩) in order to lower the quality factor Q of the resonator. For continuous wave (CW) EPR/ENDOR measurements the Q of the resonator should be as high as possible (loaded quality factor, Q_L = 2600) and a large field modulation amplitude should be achieved (1 mT). For this application a second resonator body was built from high density graphite. The cylinder (Fig. 1, part ⟨4⟩) was polished and gold coated from the inside using electro plating. The graphite body allows a 100 kHz skin depth of 5.8 mm (at room temperature) while the wall thickness was not more than 1.5 mm. Therefore, the modulation field produced by the external coils was virtually undamped. Later in the development process a third "multi-purpose" (CW and pulse EPR) body was constructed from iron-free brass with three deep slots (0.2 mm) in order to suppress the Eddy-currents generated by the modulation coils. Also in this resonator (Q_L = 1300–2600), the modulation field was virtually undamped. This body, however, does not contain an optical window.

Both plungers (Fig. 1, parts ⟨3⟩ and ⟨5⟩) were made from iron-free brass. In the plunger heads a 3.2 mm hole for the sample tubes was machined as well as 0.8 mm holes for the four silver ENDOR posts (Fig. 1, part ⟨2⟩) which were electrically insulated from the plunger by 0.1 mm PEEK (polyether ether ketone) sealing tubes. The upper plunger was movable to allow for frequency tuning. The lower plunger was fixed to the resonator and contained the contact plate for connecting the ENDOR posts to the RF line. The RF power was delivered to the ENDOR coil through 2.8 mm semi-rigid coax lines which were firmly clamped to the resonator assembly and soldered to the contact plate. The resonator body itself was attached to the Ka-band (WR28) coupling waveguide (Fig. 1, part ⟨11⟩). The iris was machined into the flattened side of the cavity

[1] The same (sealed) quartz 3 mm o.d. tube can also be used in our EPR setup at 244 GHz [21] in a non-resonant sample holder.