EPR spectra detection by heat release using PVDF films

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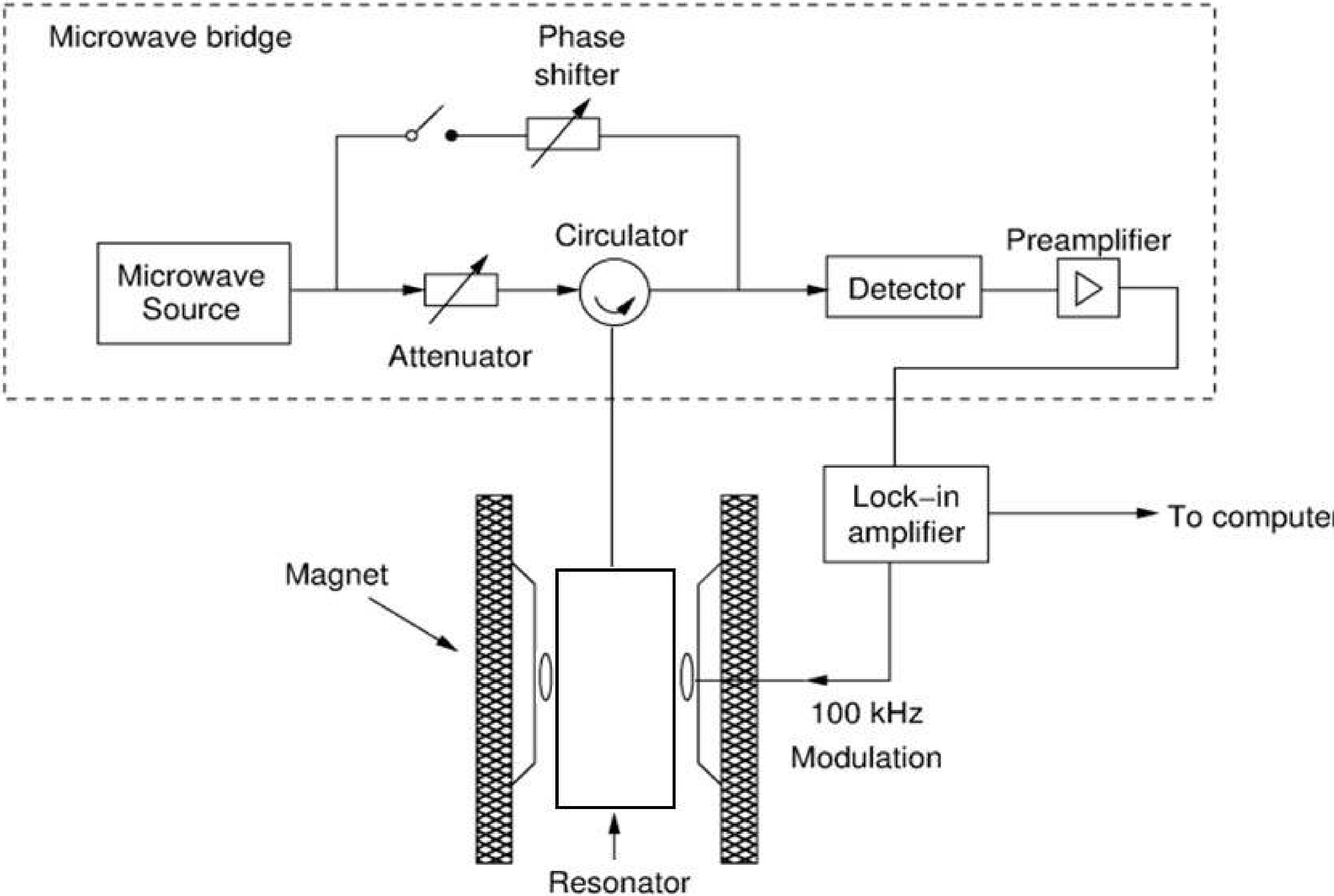
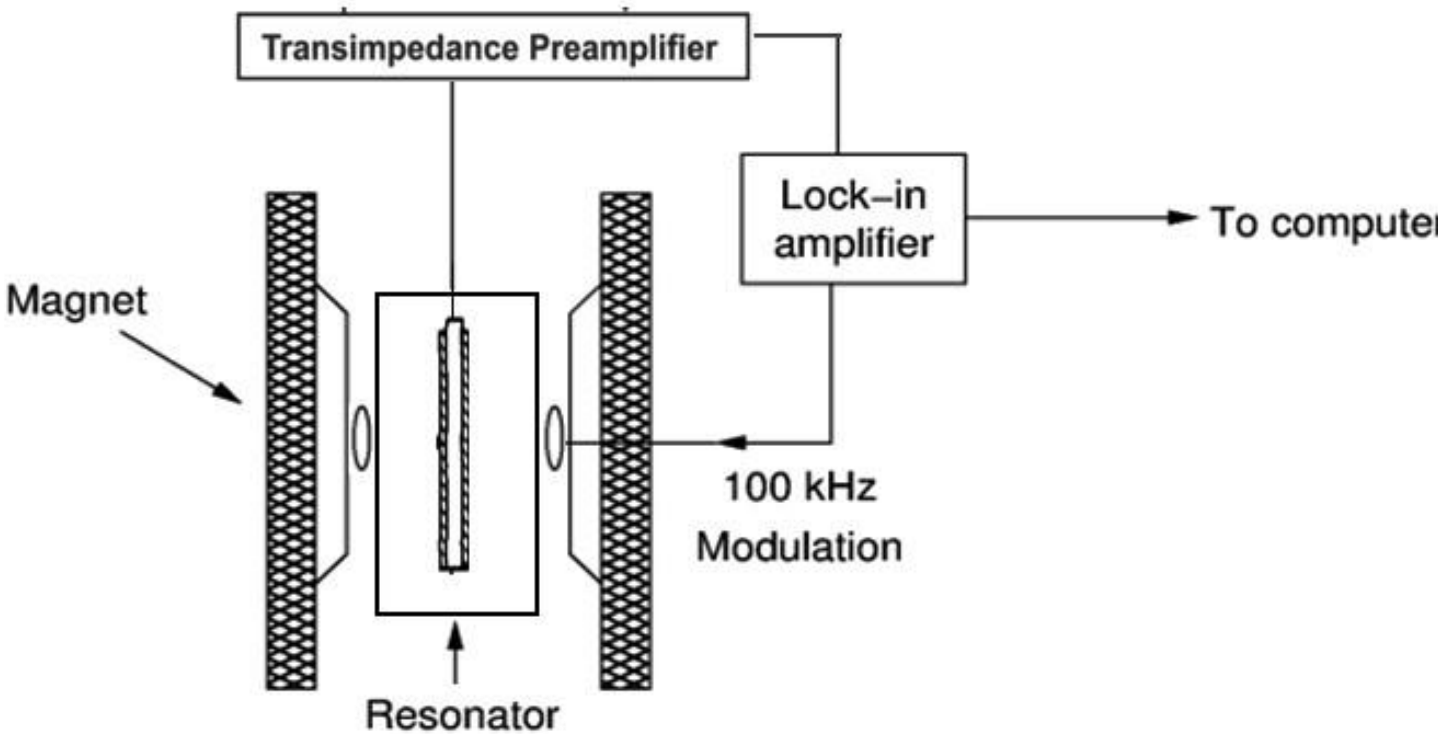

Microwave bridge
Phase
shifter
Circulator
Preamplifier
Microwave
Source
Detector
Attenuator
Lock–in
amplifier
To computer
Magnet
100 kHz
Modulation
Resonator



Transimpedance Preamplifier
Lock–in amplifier
To computer
Magnet
100 kHz Modulation
Resonator

Schmidt, J.; Solomon, I. High-Sensitivity Magnetic Resonance by Bolometer Detection. J. Appl. Phys. 1966, 37, 3719–3724.

Melcher, R.L. Thermoacoustic detection of electron paramagnetic resonance. Appl. Lett. Phys. 1980, 37, 895–897.

Melcher, R.L.; Arbach, G.V. Pyroelectric detection of magnetic resonance. Appl. Phys. Lett. 1982, 40, 910–911.

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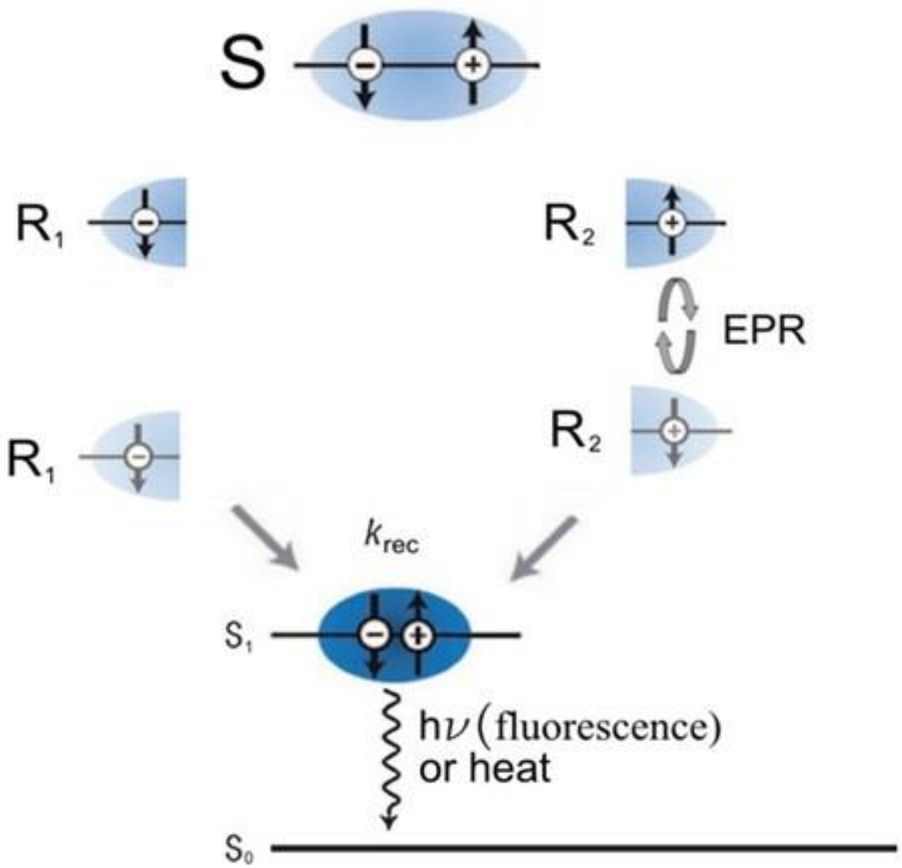
DuVarney, R.C.; Garrison, A.K.; Busse G. Electron paramagnetic resonance spectroscopy with photothermal and optoacoustic detection. Appl. Phys. Lett. 1981, 38, 675 – 676.



Direct detection EPR

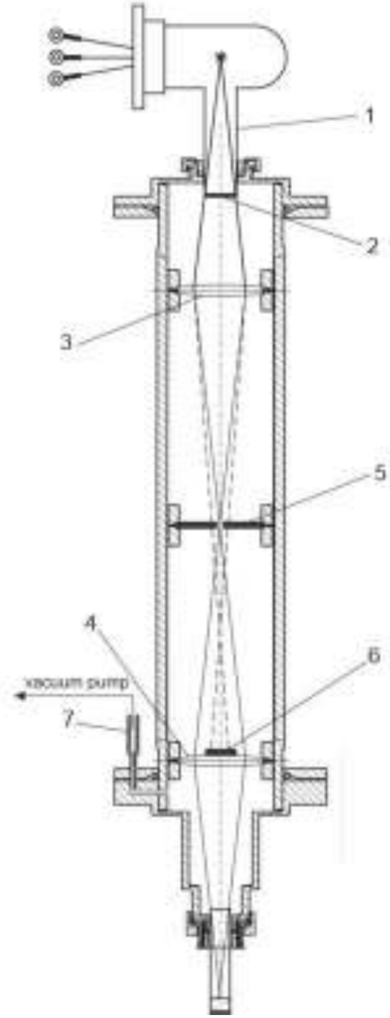
$\Delta E \sim 4 * 10^{-5}$ eV $\Delta N \sim 10^{-3}$

for X-band at room temperature

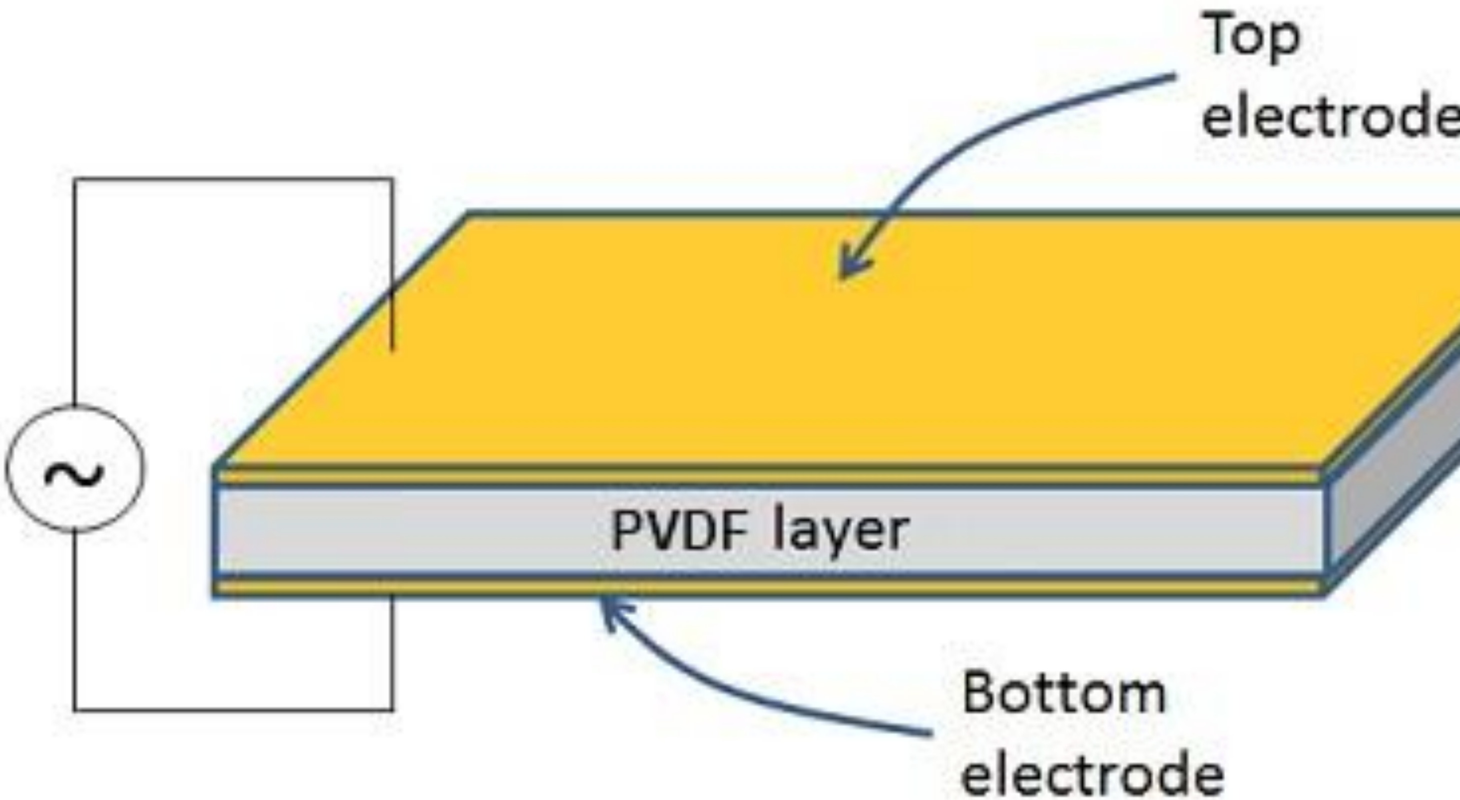
Indirect detection EPR
(RYDMR version)

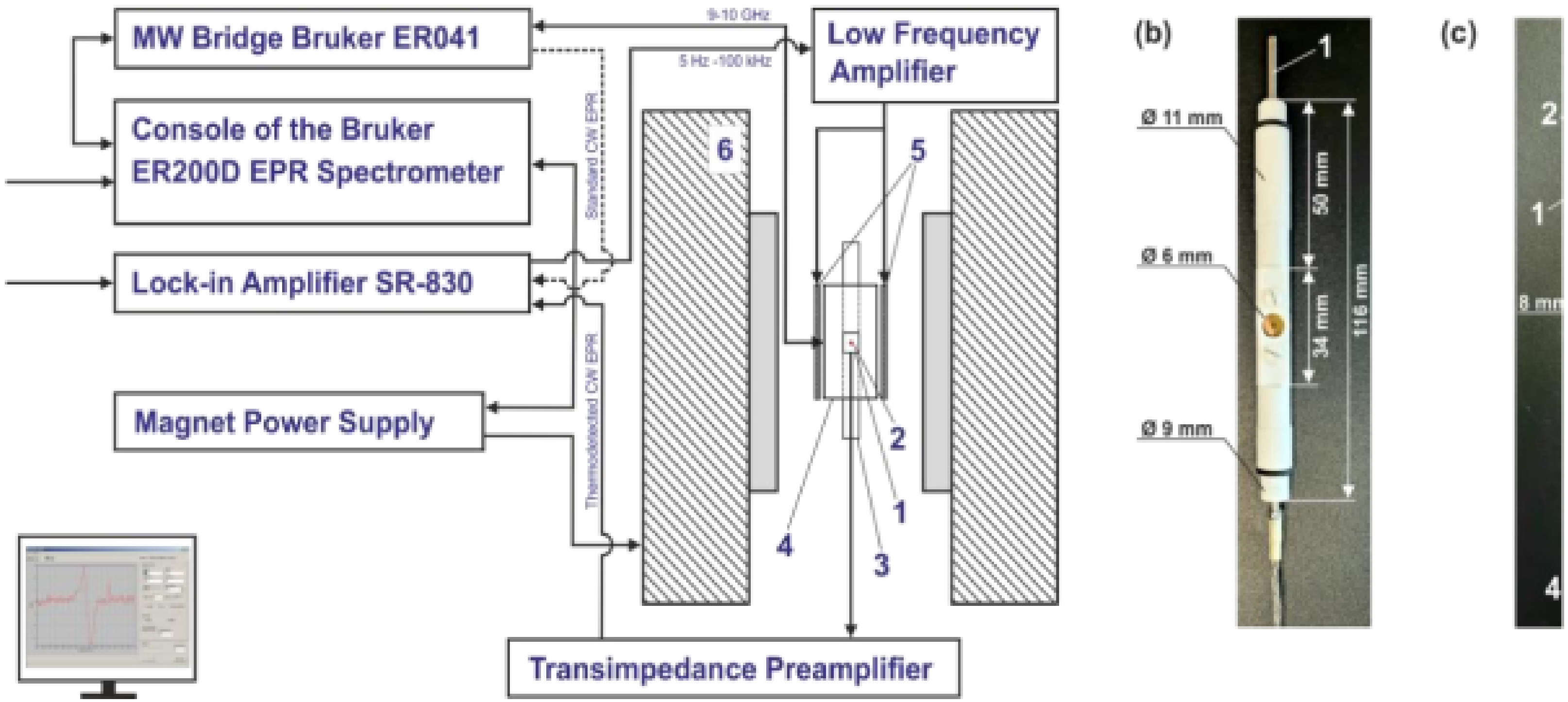
$\Delta E \sim 1$ eV $\Delta N \sim 1$

$t_{rec} < T_1$

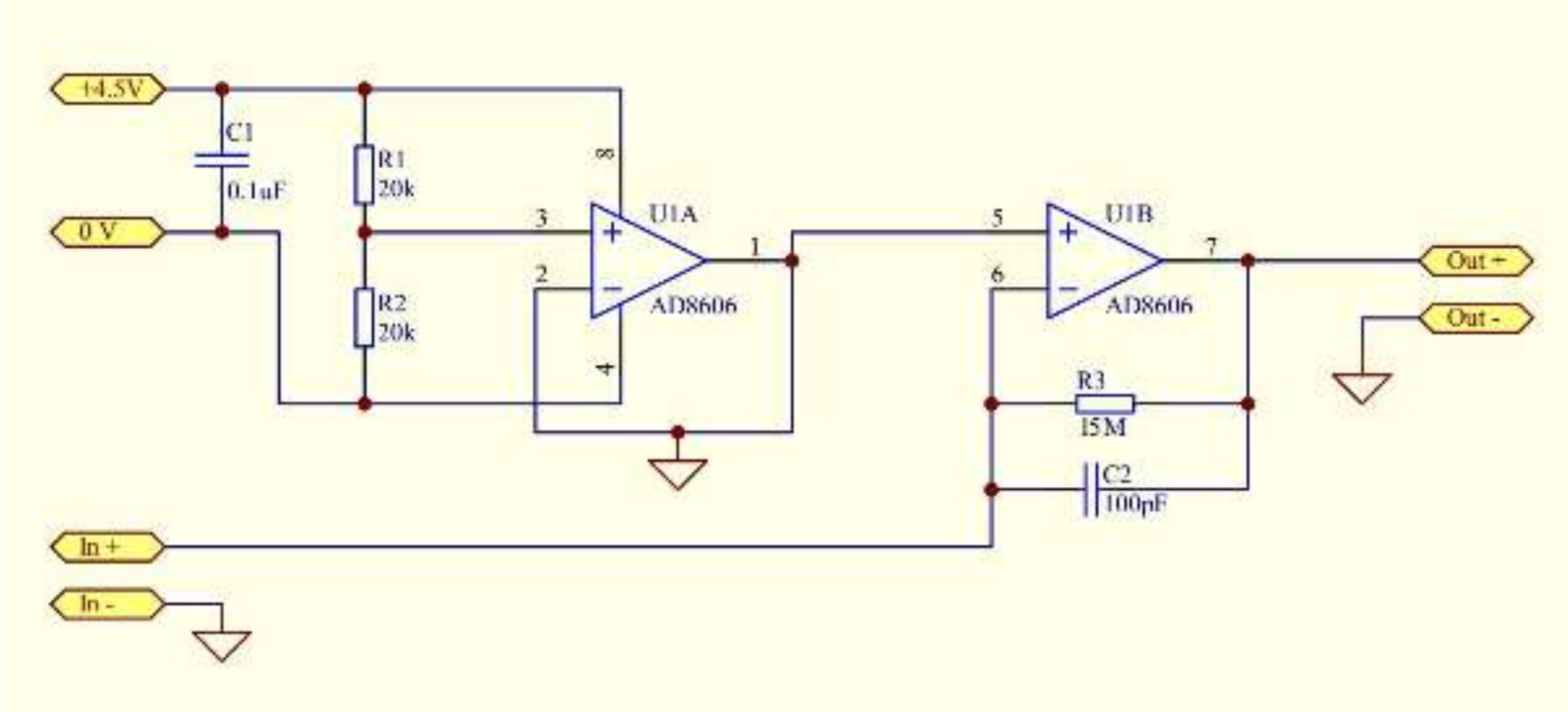


VUV Setup scheme. 1 –the lamp HAMAMATSU L7293-50, 2 - MgF2 window of the lamp, 3 and 4 - MgF2 lenses, 5 and 6 - diaphragms, 7– nipple of vacuum pump.


Top
electrode
~
PVDF layer
Bottom
electrode



(a) General scheme of the experimental setup for recording pyrodetected or standard X-band CW EPR spectra. Numbers show: (1) PVDF film—an active element, (2) sample, (3) PTFE holder, (4) Radiopan RCX 661A X-band cylindrical resonator, (5) modulation coils, (6) magnet; (b) photograph of the PVDF based detector inside the PTFE holder. The number shows: (1) ventilation tube; (c) photograph of the disassembled detector. Numbers show: (1) DPPH sample, (2) Au coated PVDF film, (3) electrical contacts, (4) ventilation tube. The ventilation tube was made for future experiments and is currently not in use.



Schematic diagram of the transimpedance preamplifier.

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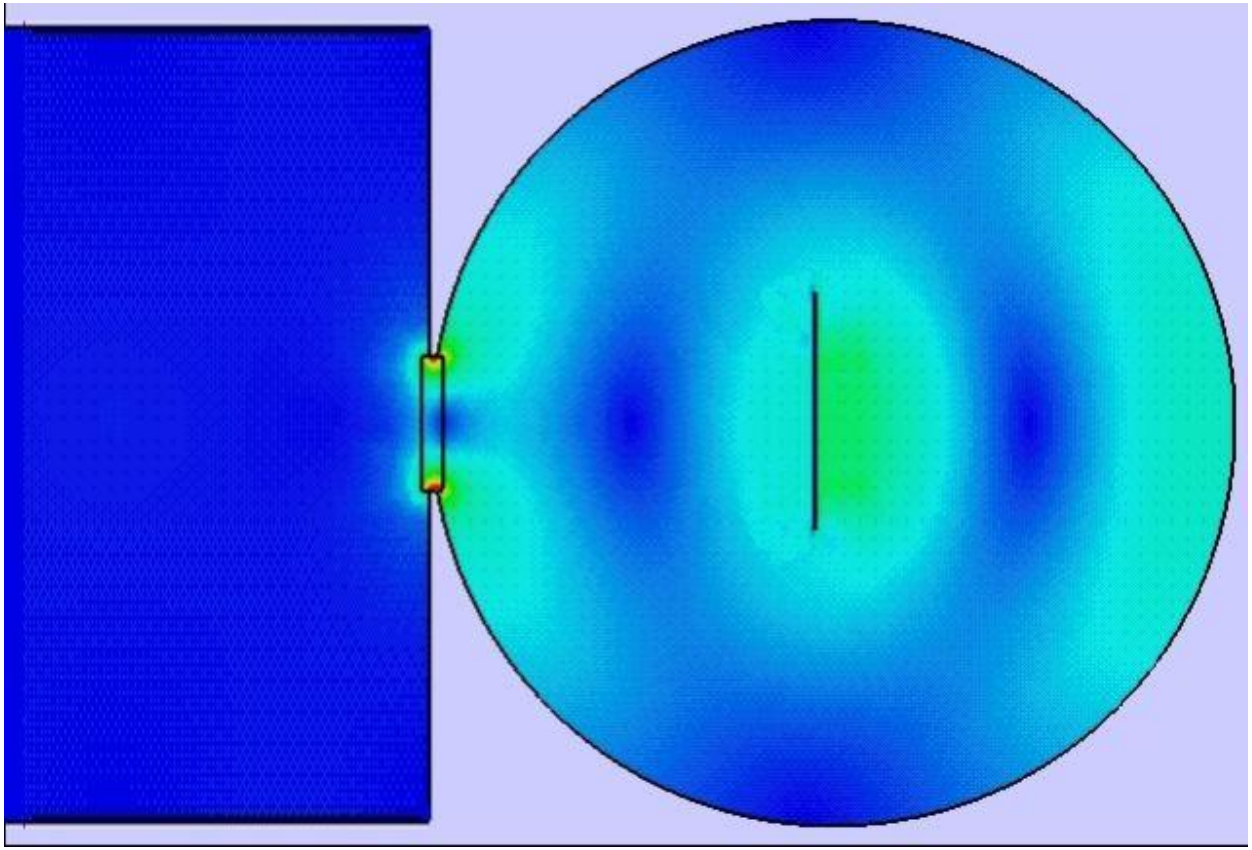


The distribution of the field amplitude H1 in a cylindrical resonator (TM110 mode) when a metal disk (shown from the edge) is placed in its center in a vertical orientation. An increase in amplitude corresponds to an increase in color brightness. (The view from one pole of a magnet to the other).

The active element of the sensor was based on commercial pyroelectric poled PVDF films manufactured by PolyK (PolyK Technologies, Philipsburg, PA, USA) with pyroelectric coefficient of about 30 μC/K*m2.

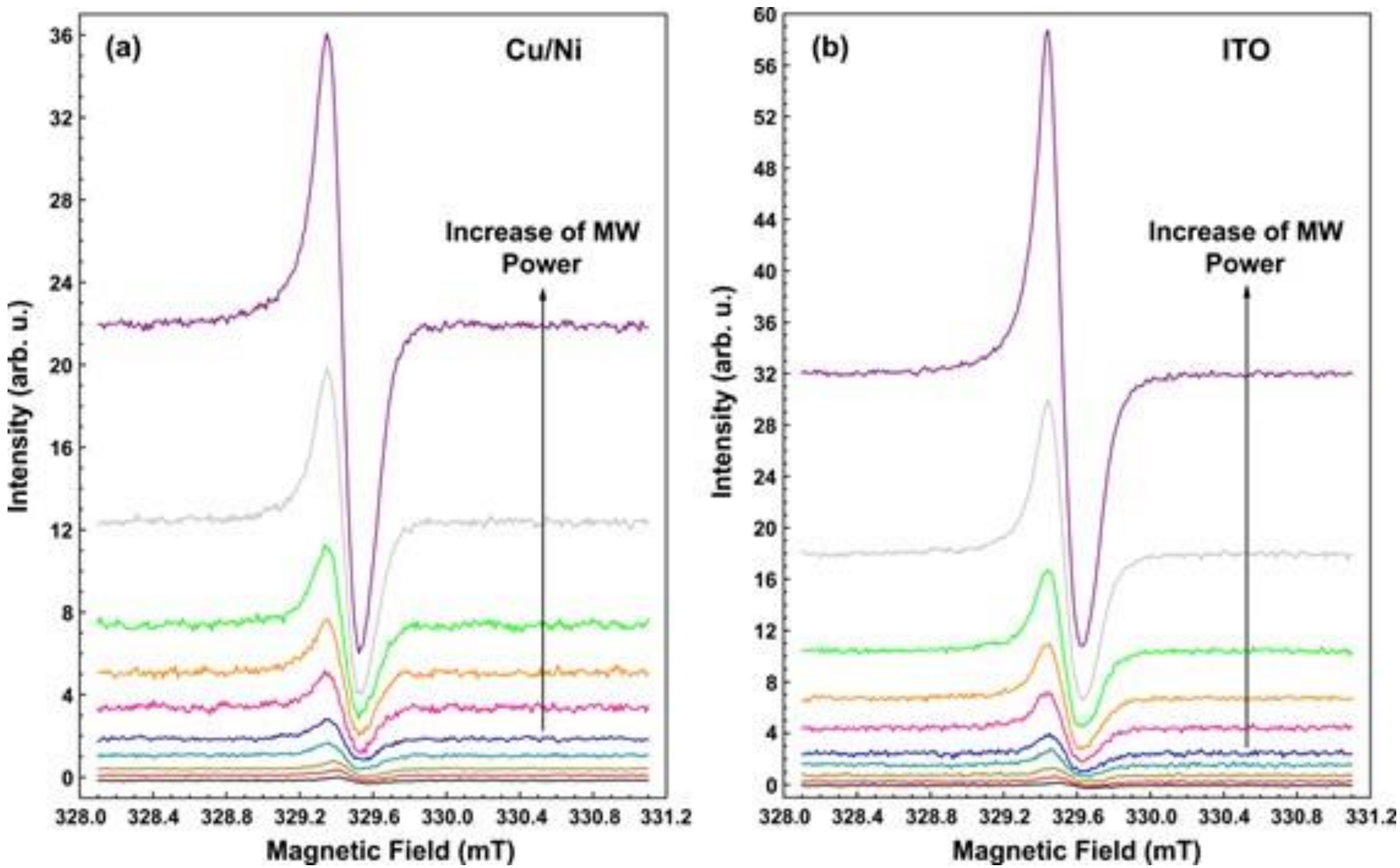
The following 3 different films were used:

(i) 28 μm thick film with 70 nm Cu + 10 nm Ni electrodes sputtered on both surfaces; sheet resistivity is equal to 1 Ω/sq,

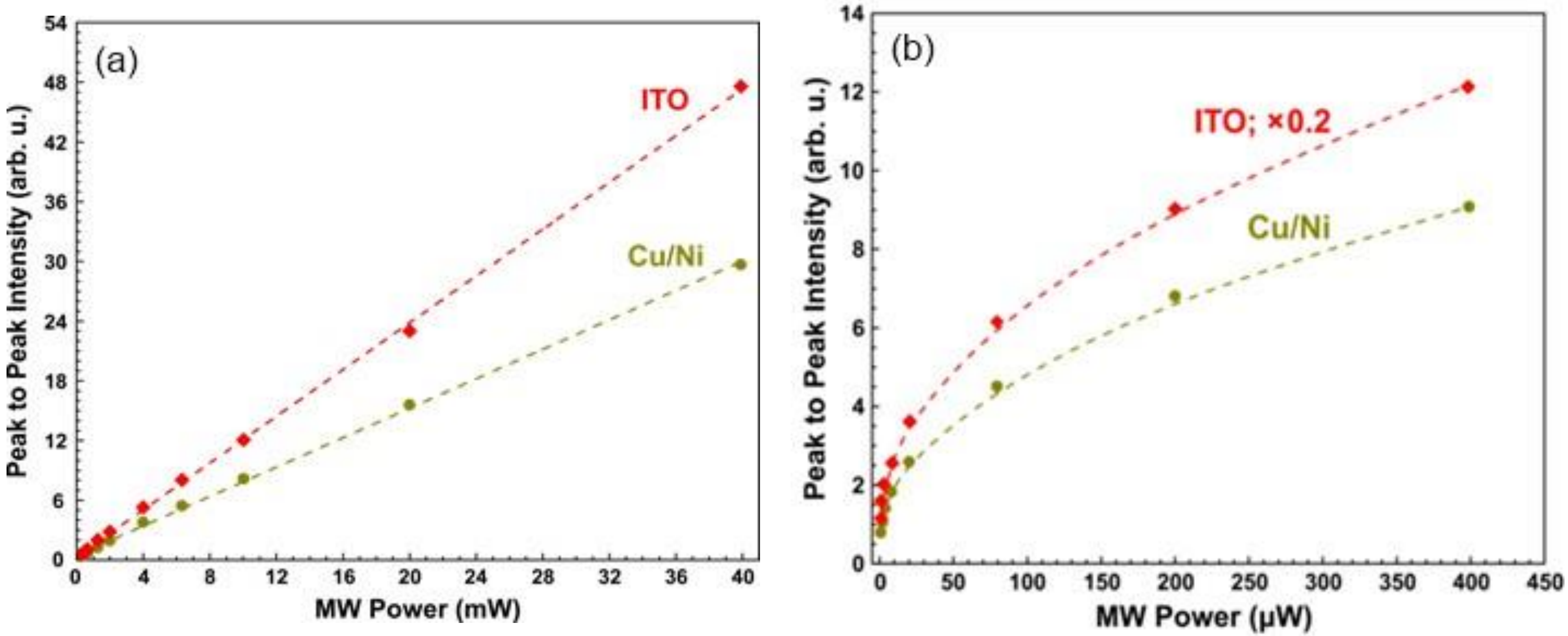
(ii) 28 μm thick film with an unspecified thickness of ITO electrodes sputtered on both surfaces; sheet resistivity is equal to 300 Ω/sq,

(iii) 12 μm thick film with an unspecified thickness of Au electrodes sputtered on both surfaces; sheet resistivity is equal to 1 Ω/sq.

For measurements, rectangular pieces of PVDF with a size of 10 × 9 mm were usually used. The sample was directly glued to the cut piece.

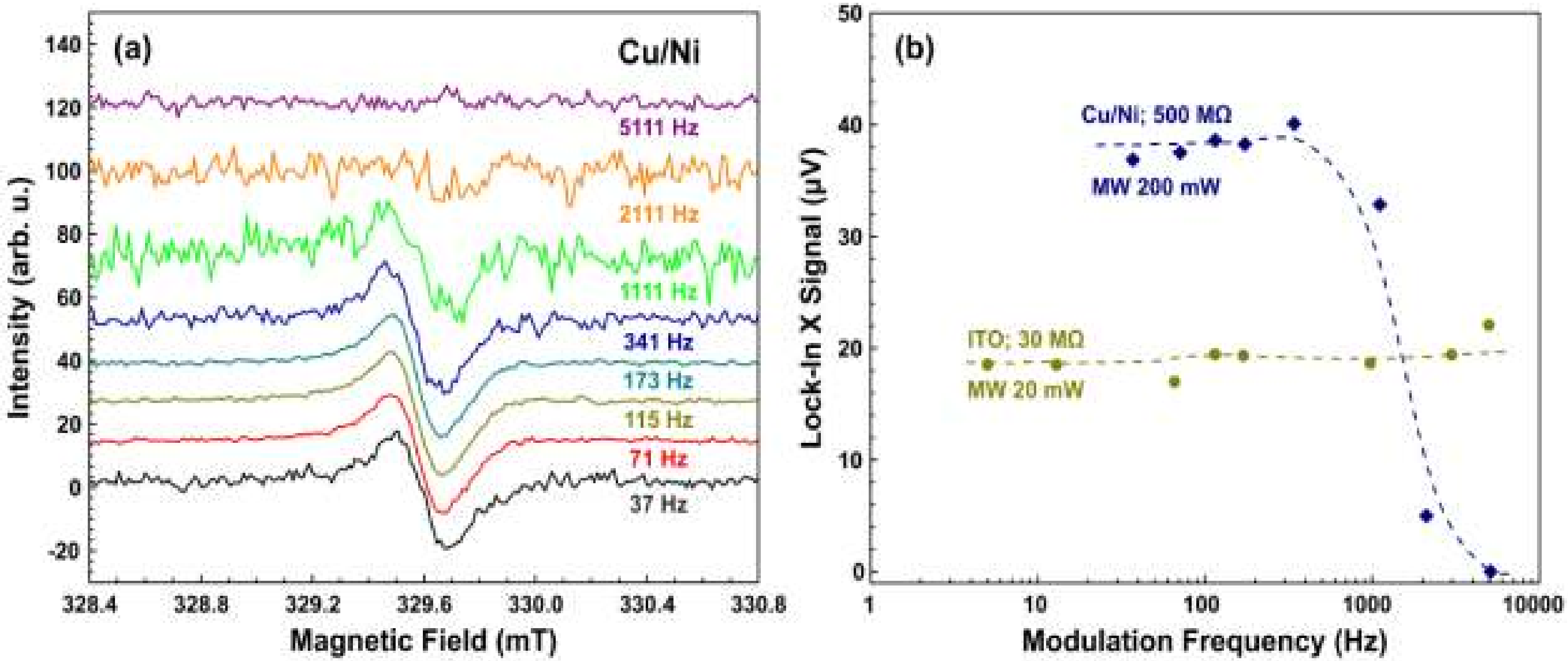


(**a**) EPR spectra of DPPH powder registered by a pyrodetector based on an active element with Cu/Ni coating at different MW power in the range of 0.2 mW (lower curve) to 40 mW (upper curve). The thickness of PVDF film is 28 μm. The amplitude of field modulation is 0.15 mT, the modulation frequency is 115 Hz, the time constant is 0.3 s, the temperature is 298 K. DPPH weight is 1.08 mg (about 1.6×10^{18} spins). The spectra are vertically shifted for better visibility. (**b**) The same with an ITO-coated active element. DPPH weight is 1.01 mg (about 1.5×10^{18} spins).

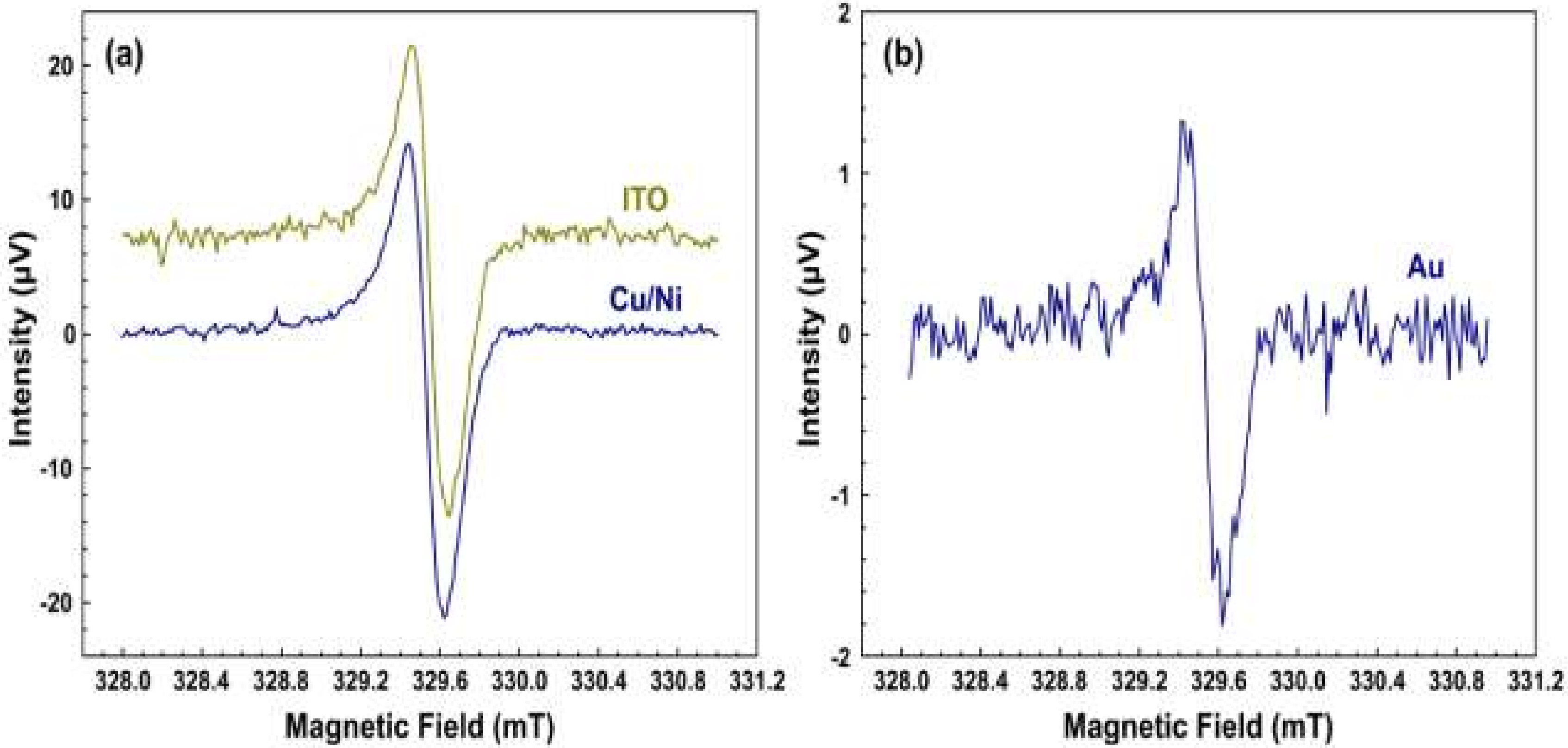


(a) MW power dependency of the peak-to-peak intensity of shown on the previous slide EPR signals. Red rhombuses and dark green circles correspond to the detection by Cu/Ni, or ITO-coated active elements, respectively. Red and dark green dashed lines show the best linear fit.

(b) MW power dependency of the peak-to-peak intensity of standard CW EPR signals. Red rhombuses and dark green circles correspond to the DPPH powder, glued to Cu/Ni or ITO (multiplied by 0.2) active elements, respectively. The thickness of PVDF film is 28 µm. Modulation amplitude is 0.15 mT, modulation frequency is 115 Hz, time constant is 0.3 s, MW power is varied in the range of 0.8 µW to 0.4mW, temperature is 298 K. The assembly (active element with glued DPPH powder and PTFE holder) was the same as in the pyrodetected measurements (see Figures 2, 3). Dashed lines are guides to the eye.



(**a**) EPR spectra of DPPH powder registered by the pyrodetector based on an active element with Cu/Ni coating at different MFs. The thickness of PVDF film is 28 μm. The amplitude of field modulation is 0.15 mT, modulation frequencies are in the range of 37 to 5111 Hz, the time constant is 0.3 s, MW power is 200 mW, the feedback resistor in the transimpedance preamplifier has the resistance (R_f) of 500 MΩ, the temperature is 298 K. DPPH weight is 2.2 μg (about 3×10^{15} spins). The spectra are vertically shifted for better visibility. (**b**) Modulation frequency dependency of the peak-to-peak intensity of the pyrodetected EPR signals for R_f equals to 500 MΩ (Cu/Ni coating, data from (**a**), dark blue rhombuses) and 30 MΩ (ITO coating, DPPH weight is 1.01 mg, dark green circles, MW power is 20 mW, other experimental parameters are the same as for Cu/Ni coating). Dashed lines are guides to the eye.



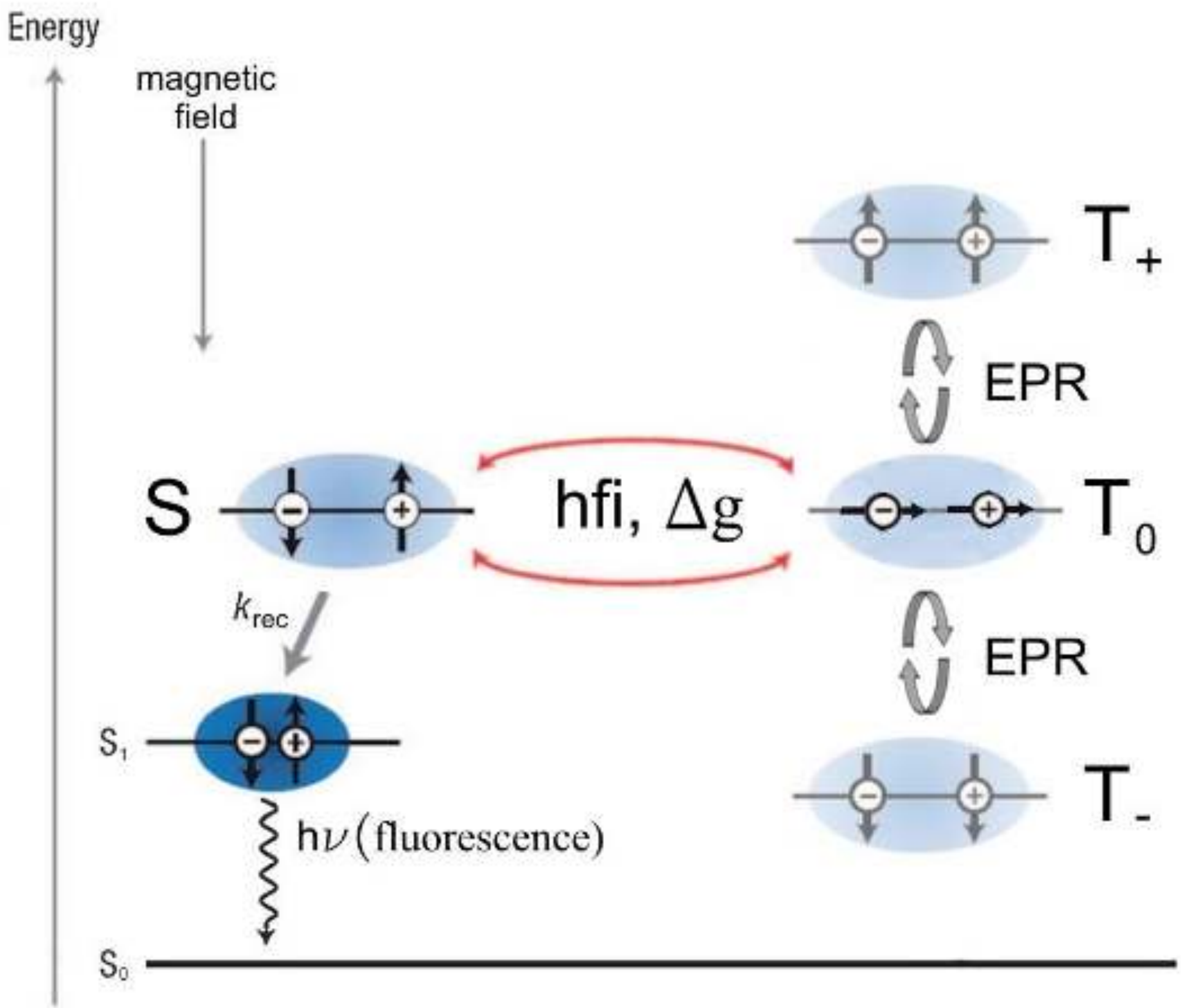
(**a**) EPR spectra of DPPH powder registered by the pyrodetector based on an active element with Cu/Ni (dark blue) or ITO coating (dark green, vertically shifted). The thickness of PVDF film is 28 μm. The amplitude of field modulation is 0.15 mT, the modulation frequency is 115 Hz, the time constant is 0.3 s, MW power is 200 mW, the temperature is 298 K. DPPH weight is 2.2 μg (about 3×10^{15} spins) and 2.8 μg (about 4×10^{15} spins) for Cu/Ni and ITO coating, respectively. Spectrum recording time is 400 s (Cu/Ni coating) and 1280 s (ITO). (**b**) The same as (**a**) for an active element with Au coating. The thickness of PVDF film is 12 μm. DPPH weight is 0.23 μg (about 3×10^{14} spins). Spectrum recording time is 2000 s.

Active Element Coating	$10^9 \times NEP$ ($W/\sqrt{Hz}$) [b]	$10^{-6} \times D^*$ ($cm\sqrt{Hz}W^{-1}$)
Cu/Ni	230	4.2
Au	300	3.2
ITO	1260	0.8

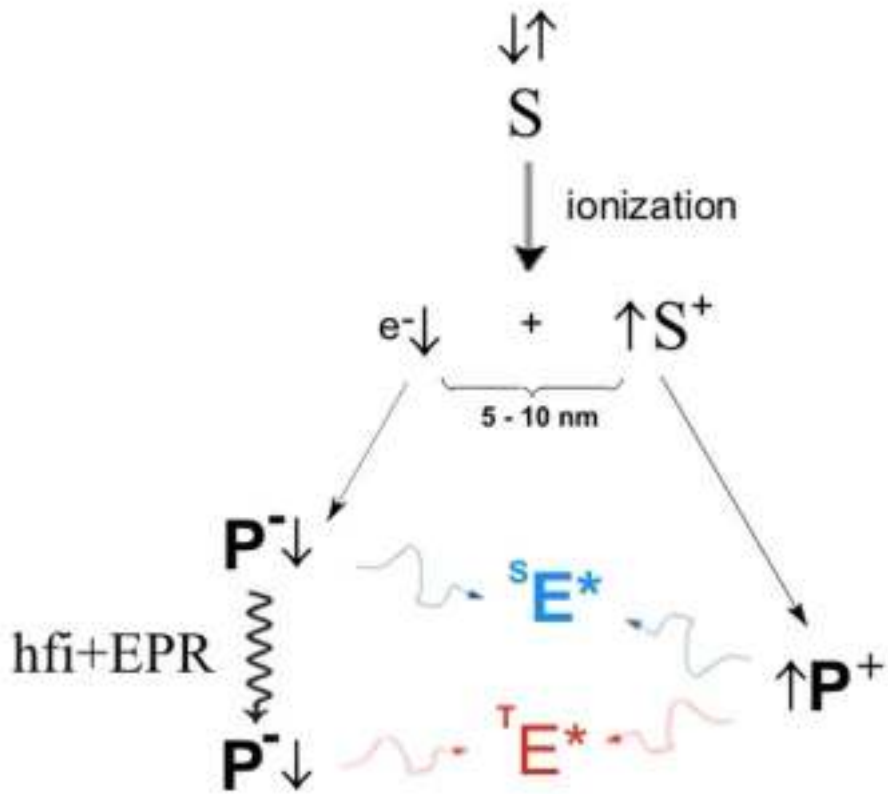
The NEP value, is 230 nW or 1.6×10^{12} eV/s. EPR signal gives less than 1% of the total number of generated pairs. So, the rate of their generation should be at least 1.6×10^{14} s^{-1} to be able to register them. To provide this rate the power of radiation absorbed by the sample should be about 1.6×10^{15} eV/s or 200 μW. Our lamp provides less than 20 μW.

So, we need to increase sensitivity 10 – 100 times

- Thank you for attention


Energy
magnetic field
T_+
EPR
S
hfi, Δg
T_0
k_{rec}
EPR
S_1
T_-
hν (fluorescence)
S_0

Pair of spin-correlated polarons



P^- is: e_s^- (stabilized electron) or A^- (acceptor anion)

P^+ is: S_s^+ (stabilized hole) or D^+ (acceptor cation)

E^* is: S^*(exiton) or A^* or D^*