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Review

Development and Application of THz Gyrotrons for Advanced Spectroscopic Methods

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Abstract: Nowadays, gyrotrons are used in numerous and diverse fields of research and technology. Their most prominent application is to electron cyclotron resonance plasma heating and current drive-in reactors for controlled thermonuclear fusion. Another matured field is the thermal microwave treatment of materials in industrial-grade gyrotron-based technological systems. The unique spectral properties of gyrotron radiation, frequency tunability, and the possibility for precise control and modulation of both the output power and frequency have made the gyrotrons attractive and appropriate radiation sources for various novel advanced spectroscopic techniques. Among them are ESR (electron spin resonance), NMR-DNP (nuclear magnetic resonance with a signal enhancement through dynamic nuclear polarization), XDMR (X-ray detected magnetic resonance), acoustic molecular spectroscopy, as well as high-precision spectroscopy for measuring the SFS (super-fine splitting of the energy levels of positronium). In this review paper, we present both the current status and the most remarkable recent achievements of these methods implemented in gyrotron-based spectroscopy systems and discuss the main trends in the development of their dedicated radiation sources operating in the THz frequency range.

Keywords: gyrotrons; spectroscopy; ESR; NMR-DNP; XDMR; molecular spectroscopy; positronium

Citation: Sabchevski, S.; Glyavin, M. Development and Application of THz Gyrotrons for Advanced Spectroscopic Methods. *Photonics* **2023**, *10*, 189. https://doi.org/10.3390/photonics10020189

Received: 14 January 2023
Revised: 6 February 2023
Accepted: 9 February 2023
Published: 10 February 2023

1. Introduction

Recent advances in gyrotron development have extended their operational capabilities into the THz frequency range, where they are among the most powerful sources of coherent radiation. This, along with many other advantageous features that will be discussed below, has opened up many new applications in fundamental physics research and high-power THz technologies. By far, the most prominent of these is the electron cyclotron resonance heating (ECRH) and current drive (ECRCD) of magnetically confined plasmas in various reactors for controlled thermonuclear fusion (e.g., tokamaks and stellarators). Another application that has become an industrially viable technology, is the microwave thermal treatment of materials (for example, ceramic sintering).

Gyrotrons are not only the most powerful sources of coherent radiation in the sub-THz to THz frequency range, but also have many other advantageous properties that make them suitable for many applications in broad areas of science and engineering. The current state of the art is well presented in the report [1], which includes a comprehensive database and list of publications on the subject that is updated annually. It shows that gyrotrons currently cover a wide parameter space of output parameters operating in CW or pulsed regimes. The main trends in recent years have been the advancement to higher frequencies and the improvement of performance (especially stabilization and precise frequency control of the generated radiation). Examples of numerous applications of gyrotrons can be found in many recent review articles [2–9].

In this paper, we specialize in gyrotron-based spectroscopy techniques and systems.

The following advantageous features of the gyrotrons make them appealing and appropriate radiation sources for various advanced spectroscopic techniques [5]. Generated

radiation possesses excellent spectral characteristics [10–12] such as narrow line width, and small frequency down- and up-shift during long time periods of CW (continuous wave) and pulsed operation. Moreover, it has been demonstrated that extremely high stability of both the power and frequency can be reached by PID control [13–16], phase locking [17–19], using reflections from an optimal external load [20–22], or just by controlling the operational parameters [23]. A record frequency stability of up to 1 Hz by a phase-lock loop in the anode voltage control has been reported recently [16]. The relative width of the frequency spectrum and the frequency stability obtained for a 0.263 THz/100 W gyrotron were 4×10^{-12} and 10^{-10}, respectively.

Frequency tunability is necessary for practically all spectroscopic techniques. In the gyrotrons, both step-wise and continuous frequency tunability are possible [24–26]. Additionally, there are means for the easy modulation of the output power and frequency [27–30]. Most of the tubes for spectroscopy are equipped with internal mode converters that produce well-collimated Gaussian-like wave beams that can be coupled to the spectrometer using waveguides or steered and transmitted using quasi-optical systems with reflectors and phase-correcting mirrors. As an attractive possibility for enhancing the efficiency and frequency bandwidth, a Gyro-TWT (traveling wave tube) with a helical operating waveguide has been proposed [31,32].

The design of a broadband output window for multifrequency and frequency-tunable gyrotrons used for spectroscopic applications is always a challenging task. This important component must provide operation at different frequencies with minimal reflection, maximum transmission, and reliable operation with minimum losses. The best, albeit expensive, material for the output vacuum window is CVD (chemical vapor deposited) diamond, which has perfect mechanical, dielectric, and thermophysical properties. Water-edge-cooled synthetic diamond disk windows used in fusion gyrotrons enable multi-megawatt power output. Another, less expensive material is silicon nitride, which is used in the less powerful gyrotrons for spectroscopy. There are several approaches to designing a broadband window. The most efficient type is a Brewster angle diamond window brazed circularly or elliptically to copper cuffs. If the RF beam, which is linearly polarized in the plane of reflection, is injected at such an angle, there is no reflection in a wide frequency range. Other types include double-disk windows (with controllable spacing between the disks), windows having disks with antireflection surface grooves, and traveling wave arrangements with two diamond disks and two mirrors.

Although gyrotrons are bulky vacuum tubes (the largest component being the superconducting magnet) they are much smaller than accelerator-based sources (e.g., free-electron lasers) and can be easily embedded in various laboratory infrastructures. In addition, a number of compact (tabletop) gyrotrons using cryogen-free magnets have been developed in recent years (see, for example, [33–35].

In the following sections, we overview some of the most prominent gyrotron-based spectroscopic techniques and conclude the paper with an outlook on their further development.

2. High-Resolution Radio-Acoustic Molecular Spectroscopy

Molecular spectroscopy naturally requires coherent radiation sources in the sub-THz and THz frequency ranges, since the rotational energy levels of molecules naturally fall within this spectral region. However, they must meet stringent requirements, such as spectral purity, frequency calibration, broad tunability, and convenience and reliability [36]. The modest power requirements of the molecular spectroscopy systems allow the use of low-power radiation sources (e.g., solid-state devices, BWOs, Smith–Purcell oscillators, etc.). However, in such a case, highly sensitive detectors are needed. Therefore, a trade-off between the output power level and other characteristics of the radiation is inevitable. In this regard, a number of studies have demonstrated the advantages of gyrotrons [5,37,38]. Here, we summarize some of the most recent advancements in various gyrotron-based systems for molecular spectroscopy.

The technique that provides the highest sensitivity uses RAD (radio acoustic detector) with BWO as a radiation source. Since the RAD sensitivity, however, is proportional to the applied microwave power, the gyrotrons offer further opportunities for its increase. Moreover, by using gyrotrons with a phase-locking loop (PLL) for fine frequency control, highly exited vibration states of molecules, forbidden transitions of non-polar molecules and very weak lines of rare species in natural abundance can be observed [37,38]. In recent years, several gyrotrons dedicated to sub-THz spectroscopy have been developed at IAP RAS [16,39,40]

The operating principle of the RAD spectrometer (see Figure 1) is based on the photoacoustic effect, which is the formation of acoustic waves when radiation of periodically varying intensity passes through a gas. The signal $S(t)$ can be expressed as the product of the incident power of the radiation E_0, the gas absorption coefficient $\alpha(\upsilon)$, and the optical path length L.

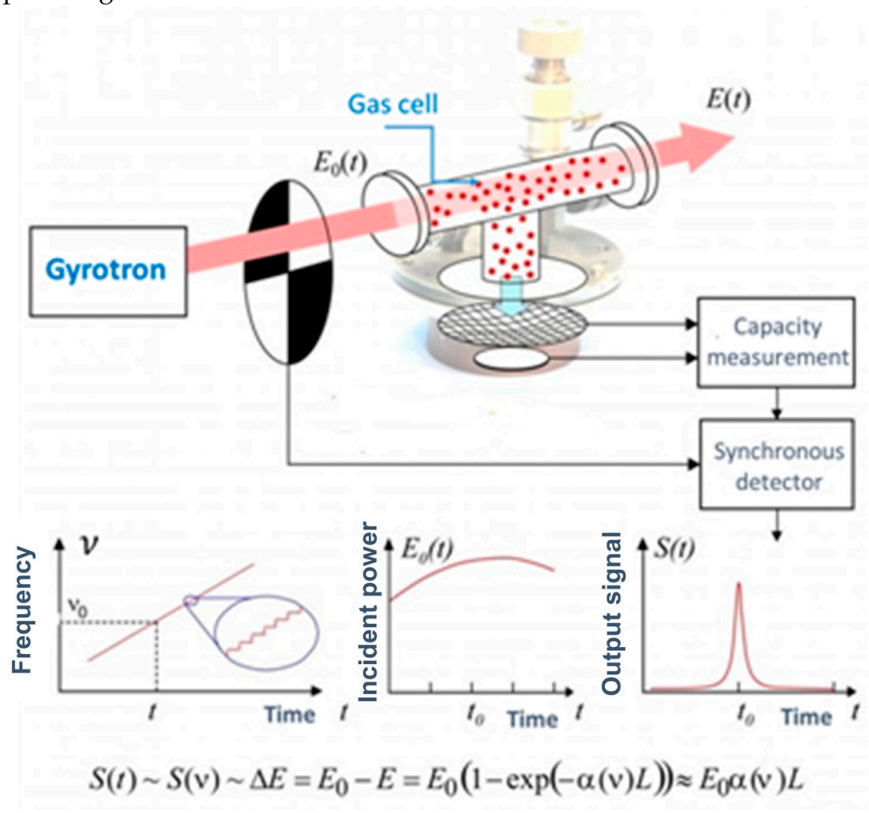

Figure 1. Principle of gyrotron-based RAD spectroscopy.

The capabilities of gyrotron-based RAD spectroscopy have recently been demonstrated using an automated facility [39]. The main components of the spectrometer are shown in Figure 2. As a radiation source, a gyrotron developed at IAP-RAS and operated in the CW regime at a central frequency of about 263 GHz and an output power of up to 1 kW has been used. The radiation frequency can be continuously tuned in an interval of 0.2 GHz by varying the electron beam voltage and the temperature of the cavity. The width of the radiation spectrum Δf is about 0.5 MHz ($\Delta f/f \sim 10^{-6}$) and is due to the fluctuations of the accelerating potential provided by the high-voltage power supply. Using sulfur dioxide (SO_2) as the test gas, which has a very dense and well-studied spectrum in the mm/sub-mm range, an absorption sensitivity of the spectrometer on the order of 6×10^{-10} cm^{-1} was achieved. These experiments have shown that an increase in the scanning radiation power of about three orders of magnitude leads to a proportional increase in the sensitivity of the RAD spectrometer [40] and therefore prove the efficiency of this so-called "power" approach.

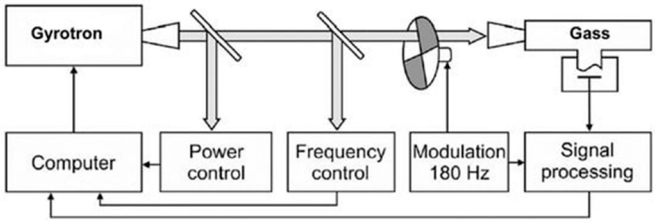

Figure 2. Schematic of a gyrotron-based radio-acoustic detection (RAD) spectrometer.

Recently, the operational performance of the gyrotron used in the RAD spectrometer has been improved significantly. Most notably, the radiation frequency has been stabilized against a reference oscillator using a phase-lock loop (PLL) system in the anode voltage control, which provides high stability, narrow bandwidth (relative width of approximately 10^{-12}), and accurate frequency control. Sample spectra have been registered at the first (263 GHz), second (526 GHz), and third (789 GHz) harmonic of the cyclotron frequency with the modulation of both the output power and frequency.

A novel concept of high-power THz radiation sources based on five-fold frequency multiplication in gyrotrons for spectroscopic applications has been proposed in [41]. An efficient excitation at the 5th cyclotron harmonic has been achieved using a specific property of the eigenmodes of cylindrical waveguides that allow satisfying the conditions for simultaneous resonances at two selected TE modes with different harmonic numbers, albite only approximately (as a matter of fact, asymptotically), but with sufficient accuracy [41,42]. The numerical experiments performed using an averaged time-domain model have shown that despite the mode competition, it is possible to excite Watt-level 1.25 THz 5th cyclotron harmonic in a recently developed sub-MW 0.25 THz gyrotron. These results open the possibility to develop a new generation of advanced radiation sources for high-resolution molecular spectroscopy.

It should be mentioned that as the amplitude of the incident radiation increases, the transition probability tends to saturate and the absorption constant decreases. Such nonlinear absorption is a result of the change in population of eigenstates of the molecule by the strong radiation. Furthermore, the high power of the gyrotron radiation (on the order of several kW) could lead to nonlinear polarization of the medium and thus to the possibility of observing a range of nonlinear phenomena that can be exploited in novel yet unexplored spectroscopic techniques.

3. Gyrotron-Based ESR Spectroscopy

ESR (electron spin resonance) spectroscopy, also known as EPR (electron paramagnetic resonance) spectroscopy is a versatile, nondestructive, and very sensitive analytical technique used to study the structure and dynamics of molecules, radicals, paramagnetic ions, and other substances with unpaired electron spins. It utilizes microwave radiation to probe the studied materials placed in an externally applied static magnetic field. This method allows us to measure the Zeeman energy splitting of the electronic spin levels and to investigate, for instance, the electron spin–spin interaction, the spin–lattice relaxation, as well as the effect of the ambient substances on the spin system. The traditional ESR spectroscopy is usually performed in the microwave frequency range (9 GHz–30 GHz) and utilizes as radiation sources solid-state (semiconductor) oscillators (e.g., Gunn and IMPATT diodes) or vacuum tubes such as magnetrons, klystrons, traveling wave tubes (backward wave oscillators, orotrons, and gyrotrons [43,44]. Above 90 GHz, this technique is usually termed HF-ESR (high-field ESR) spectroscopy.

The main advantages of gyrotron-based ESR spectroscopy are the high power, frequency tunability, and stability of the radiation, enabling the investigations of complex and highly structured systems. Recently, gyrotron-based ESR spectroscopy has been extended to the THz frequency range. The utilization of higher frequencies allows for the detection of weaker signals, making the technique more sensitive and significantly increasing its

spectral resolution. The elevation of the signal-to-noise ratio leads to a shorter spectrum acquisition time. For the first time, an ESR spectrometer with a wide frequency range using a gyrotron as a radiation power source has been reported by Tatsukawa et al. [45]. This pioneering paper demonstrated both the feasibility and the potential of gyrotron-based ESR spectrometers and instigated active research on them including a steady improvement of the used instrumentation and techniques. As shown by Casper et al. [46] promising means for further increase in the sensitivity and the resolution is the usage of frequency and field-modulated sub-THz radiation. The latter approach allows the detection of weak and very broad electron spin resonances. Furthermore, in the gyrotron-based ESR spectrometers, both pulsed and CW waves can be used. In the former case, the relaxation times of electron spins can be measured as well.

In the ESR system developed at the Research Center for Development of Far-Infrared Region of the University of Fukui (FIR UF) [47], a pulsed magnetic field with an intensity of up to 30 T has been generated in synchronized phase with a pulsed gyrotron operation. The ESR spectrometer has been successfully applied to three cases of ESR measurements. In the first of them, the temperature dependence of the ESR signal has been measured for a typical antiferromagnetic material MnO at the frequency of 301 GHz. In the second case, the dependence of the fine structure constant of ruby on the magnetic field intensity has been measured in the millimeter to submillimeter wave region. In both cases, the gyrotron was operated in the regime of a complete CW mode. In the final set of measurements, a pulsed technique was applied to the ESR. The synchronization between the operation of the gyrotron and the magnet has been performed using a single pulse to trigger the high-voltage power supply of the tube while the condenser bank for powering the magnet is triggered by a delayed pulse. In the next ESR system, the pulsed magnetic field intensity has been increased further up to 40 T [48]. Using this high-field arrangement, ESR measurements have been performed at the temperature of 4.2 K in a $CsFeCl_3$ single crystal and the frequency field diagram of ESR absorptions has been obtained.

The pulsed ESR measurements described in [49] utilize as a radiation source a gyrotron oscillator operating at a frequency of 154 GHz. Its output has been sliced to intense and short millimeter wave pulses with a light-controlled semiconductor shutter. A quasi-optical transmission system transmits these short pulses to the ESR measurement probe. In this study, the FID (free induction decay) signal of BDPA radical was successfully observed. This pulsed ESR system allows the method of electron spin echo envelope modulation (ESEEM) to be used [50].

In the next improved version of the pulsed ESR spectroscopy system [51,52] the FID signal of stable radicals of BDPA diluted with polystyrene was successfully observed by the quadrature detection method. By Fourier transforming these FID signals, a high-resolution FT-ESR spectrum of BDPA was successfully obtained. In this experimental investigation, the sensitivity has been improved by digitally processing the sampled FID signal and averaging the spectrum from which unnecessary signals were removed by several Fourier transforms.

Force-detected (FD) high-frequency electron spin resonance spectroscopy conceptually is a novel broadband high-frequency electron spin resonance (HFESR) technique. In contrast to the ordinary force-detected electron spin resonance (ESR) technique, which detects the magnetization change due to the saturation effect, this method measures the magnetization change due to the change in the sample temperature at resonance [53].

Measurements of force-detected electron spin resonance (FD ESR) at 154 GHz using a gyrotron have been reported in [54]. The high output power allows the use of a strong transverse magnetic field larger than 10^{-4} T, which is sufficient to cause ESR saturation. The obtained FDESR signal is characterized by high spin sensitivity on the order of 10^{12} spins/G at a temperature of 280 K and is appropriate for studying of low-spin concentration sample. Owing to the high force sensitivity of micromechanical devices, the spin sensitivity is generally much higher than that of the transmission method. The schematic of the gyrotron FDESR system is shown in Figure 3.

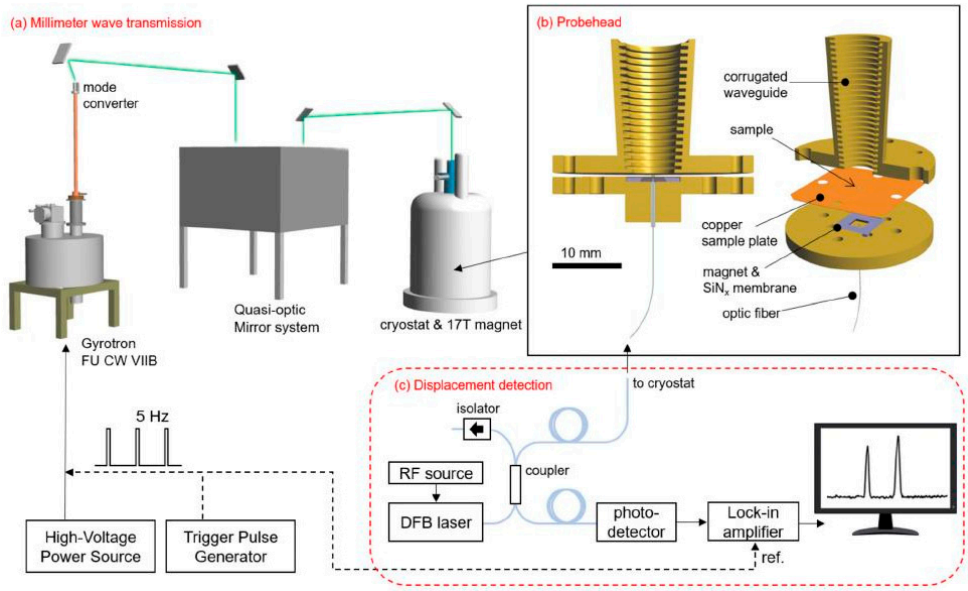

Figure 3. (**a**) Schematic of the gyrotron FDESR system. (**b**) Cross-sectional view of the FDESR probe head and part configuration. (**c**) Setup of optical interferometry for the displacement detection of the nanomembrane. Reprinted with permission of AIP Publishing from Ref. [54].

In this experimental setup, the 154 GHz gyrotron FU CW II B was operated in the pulse mode with a repetition of 5 Hz and a duty ratio of 0.1–10%. The peak and average power of the millimeter wave in the sample space were estimated to be 5 Wand 5–500 mW, respectively. Figure 3b shows the schematic of the ESR probe head. ESR signals of DPPH and CuPzN at room temperature have been obtained with spin sensitivity on the order of 10^{12} spins/G. It has been concluded that the combination with a multi-frequency gyrotron, which can generate multiple frequencies by selectively exciting the higher-order cyclotron modes inside the cavity, is a promising method to broaden the frequency range.

4. DNP-NMR Spectroscopy

Nuclear magnetic resonance (NMR) is similar to ESR, the fundamental difference being that the latter is based on the magnetically induced splitting of electronic spin states, whereas NMR is concerned with the splitting of nuclear spin states. NMR spectroscopy is a powerful analytical tool used to study a wide variety of materials (e.g., complex biomolecules, drugs, polymers, and many others), providing extensive information about their content, structure, phase changes, chemical reactions, and so on. It is revolutionizing various fields of research, especially analytical chemistry, structural biology, and materials science. Modern NMR spectrometers are highly sophisticated, complex, and expensive systems that use powerful magnets. Recently, they have achieved field strengths of up to 28 T. However, in addition to these advantages, there are some well-known disadvantages. The most important one is the low signal-to-noise ratio, which leads to low sensitivity and long times for spectrum acquisition.

All of these disadvantages have been eliminated by an advanced technique pioneered by Griffin et al. at MIT [55]. This breakthrough method provides dramatic signal enhancement (theoretical maximum amplification factor of up to 658 when the nucleus is 1 H) through dynamic nuclear polarization (DNP) and is therefore called DNP-NMR spectroscopy. In essence, it uses a polarizing agent, the electron spins of which are easily polarized, and then this large polarization is transferred to the surrounding nuclei of the material under study by irradiation with gyrotron radiation at a frequency close to that of the EPR transition. With the advance to higher magnetic fields and, respectively, to higher frequencies, this technique requires powerful radiation sources in the sub-THz range. Following spectacular advances in the development of gyrotrons covering this frequency

range, they are now considered to be the only suitable sources that also have the capacity to further increase both the output power and frequency that will be required for the next generation of DNP-NMR instruments.

Over the years, a number of gyrotrons for DNP-NMR spectroscopy have been developed at MIT [56–59], FIR UF [60–64] IAP RAS [65–67], and other institutions around the world [68–74]. Some of them are shown in Table 1.

Table 1. Gyrotrons for DNP-NMR spectroscopy.

Institution/Gyrotron	Frequency, GHz	Spectrometer
MIT	140	210 MHz (the 1st in the world)
MIT	250	380 MHz
CPI	263	400 MHz
MIT	330	500 MHz
CPI	395	600 MHz
MIT	460	700 MHz
MIT, CPI	527	800 MHz
FIR FU/FU CW IV	131	200 MHz at FIR UF
FIR FU/FU CW VII	187	300 MHz at Warwick Univ.
FIR FU/FU CW II, FU CW VI	394	600 MHz at Osaka Univ.
FIR FU/FU CW GVI FU CW GVIA	460	700 MHz
IAP-RAS	260	400 MHz at Goethe University, Germany
EPFL, Switzerland	265–530	400–800 MHz

Since the commercially available magnets for NMR have a discrete range of field strengths (and correspondingly fixed resonances), this is also true for the central frequencies of the gyrotrons used. In the following, we outline the progress in this field with some representative examples.

The most advanced gyrotrons for DNP-NMR spectroscopy are characterized by wide frequency tunability (above 1–2 GHz), high stability of both output power (<1%) and frequency (<1 ppm) over long operating times (up to weeks) in a CW mode, high mode purity, etc. The gyrotrons developed at MIT cover a wide frequency range and generate radiation at 140, 250, 330, 460, and 527 GHz, respectively [56,58]. The gyrotrons with output frequencies of 140 GHz and 250 GHz operate at the fundamental resonance of the electron cyclotron frequency, while the others operate at their second harmonic. Continuous frequency tuning in these tubes is achieved by combining various means such as varying the magnetic field, the beam voltage, and the temperature of the cavity (controlling its thermal expansion) as well as by exciting a sequence of successive and partially overlapping high-order axial modes (TEmnq, q > 1). For instance, the 330 GHz gyrotron has demonstrated a tuning band of 1.2 GHz. The second harmonic frequency-tunable gyrotron at 527 GHz is built for an 800 MHz DNP-NMR spectrometer and provides up to 9.3 W CW power at an efficiency of ~0.5% [58]. This oscillator is tunable within ~0.4 GHz by combining voltage and magnetic field variations. The gyrotron is equipped with an internal quasi-optical (QO) mode converter that produces a Gaussian-like beam that couples to the HE_{11} mode of an internal corrugated waveguide periscope assembly leading up to the output window.

In addition to the aforementioned oscillators used for polarization transfer in the CW mode, two gyro-amplifiers operating at 140 and 250 GHz have been developed for novel techniques in which polarization transfer is based on coherent processes (e.g., the integrated solid effect, the dressed-state solid effect, electron–nuclear Hartmann–Hahn

cross-polarization, etc.) that are more favorable at high magnetic fields [59]. They are intended for pulsed DNP NMR in the time domain.

The 140 GHz gyro-amplifier operates in the HE06 mode of an overmoded quasi-optical waveguide [56]. The demonstrated performance of this radiation source shows that it can be used for dynamic nuclear polarization and electron paramagnetic resonance spectroscopy amplifying pulses as short as 0.5 ns. The gyrotron traveling wave tube (TWT) amplifier at 250 GHz uses a photonic bandgap (PBG) interaction circuit. This device has demonstrated pulses of ~260–800 ps duration, a bandwidth of 8 GHz bandwidth, and 38 dB gain. With drive input from a diode of 100–200 mW, the amplifier yields 600–1200 W of output power [57].

Recently, a frequency-agile gyro-BWO (backward wave oscillator) has been reported [75]. It possesses a system of frequency control that allows chirped microwave pulses to be used in conjunction with MAS (magic angle spinning) NMR. The interaction cavity is long enough to support many pure and hybridized axial modes, yielding a continuous microwave power output over a spectral width of 0.67 GHz at a single magnetic field. The operating mode TE_{52q} mode supports continuous tuning bandwidth over a frequency range of 197.2–198.4 GHz, which can be controlled with 1 MHz precision by adjusting the electron beam voltage [75]. This radiation source is appropriate for time-domain electron decoupling and pulsed dynamic nuclear polarization.

A series of CW gyrotrons (the so-called FU CW series) have been developed at FIR UF for various applications. Their output powers and frequencies occupy broad parameter space and are used in many fields of high-power Terahertz science and technology [25,60–62,64]. Some of them are designed specially as radiation sources for spectroscopic studies. One of these is the gyrotron FU CW II, which was built using an 8 T liquid-He-free superconducting magnet (SCM) and generates radiation at a frequency of 394.6 GHz (at the second harmonic of the cyclotron frequency) that corresponds to 600 MHz proton NMR at a magnetic field intensity of about 14 T. An improved version of this tube (FU CW IIB) has demonstrated high stability of the output power (fluctuations below 0.5% during 18 h of CW operation), which was achieved by using a PID feedback control. Following the development and optimization of this tube, the gyrotron FU CW IV intended for 200 MHz DNP-NMR spectroscopy has been designed. This device uses a 10 T cryogen-free SCM. By simply changing the magnetic field in the cavity from 4.9 to 5.2 T and operating as a gyro-BWO on a sequence of high-order axial modes (HOAM) continuous tunability in a broad frequency band from 134 to 140 GHz has been achieved. The same technique for smooth frequency tunability has been applied to the gyrotron FU CW VI, which has an even stronger SCM with a maximum field intensity of 15 T. This tube has been designed as a radiation source for the 600 MHz DNP-NMR spectrometer at the Institute for Protein Research (IPR) at Osaka University. One of the most versatile tubes, namely FU CW VII, can be used for both 300 and 600 MHz DNP-NMR generating radiation with frequencies of 200 GHz (fundamental operation) and 400 GHz (second harmonic), respectively. By varying the electron beam parameters and the magnetic field many operating modes can be excited in this gyrotron allowing step tunability over a wide range from 86 to 223 GHz. So far, the above-mentioned radiation sources have been used in several DNP-NMR spectrometers: (i) 200 MHz with FU CW IV at FIR UF; (ii) 300 MHz with FU CW VII at Warwick University; (iii) 600 MHz with FU CW II and FU CW VI); and (iv) 700 MHz with FU CW GO-I and FUCW GO-II.

Advanced instrumentation for DNP-enhanced MAS NMR spectroscopy using the radiation sources developed at FIR UF was presented in [62]. They provide continuous frequency tuning and fast frequency modulation for the 395 GHz–600 MHz and 460 GHz–700 MHz DNP NMR spectrometers. The latter system (700 MHz) includes two gyrotrons (FU CW VI and FU GO II, operating at 395 GHz and 460 GHz, respectively), and a quasi-optical transmission system that combines two independent submillimeter waves into a single dichromic wave [62]. The diagram of this system is presented in Figure 4. Two cryogenic MAS NMR probe systems have also been developed, operating at ∼100 K

and ~30 K, respectively. The last-mentioned system utilizes a novel closed-loop helium recirculation mechanism, achieving cryogenic MAS without consuming any cryogen. In the experiments, two orders of magnitude sensitivity gain at 40 K and 16.4 T has been achieved.

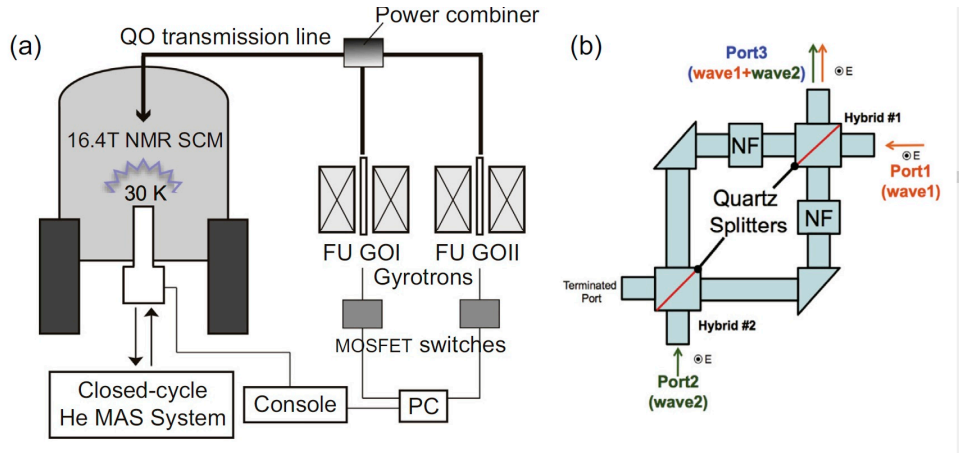

Figure 4. (**a**) Diagram of 460 GHz-700 MHz DNP-NMR spectrometer with two gyrotrons. Two sub-millimeter waves (SMMWs) can be independently delivered to a DNP MAS NMR probe. MAS is performed with a closed-loop helium circulation system. (**b**) A diagram for the custom-designed beam combiner for SMMWs, based on the corrugated waveguide sections, a set of 3 dB-hybrids, and tunable Notch filters. Reprinted with permission of Elsevier from Ref. [62].

Advancement towards higher frequencies, however, that are in demand for the next generation DNP-NMR systems encounters serious problems. Due to the limitations of the field strength of the currently available SCM, the gyrotrons must operate at the second harmonic. This additionally makes the inherent mode competition even more severe. A promising concept for increasing the mode selectivity (especially between the fundamental and second harmonic resonances) is to use a gyrotron with two electron beams (the so-called double beam gyrotron). Such a tube has been developed recently at FIR UF in collaboration with IAP-RAS [63]. It has been designed as a second harmonic oscillator operating at 0.79 THz with output parameters that are appropriate for the envisaged next-generation of ultrahigh field 1.2 GHz DNP-NMR spectrometers based on magnets with a field intensity of about 28.2 T.

The gyrotron for both liquid-state and solid-state NMR-DNP spectroscopy, developed at IAP-RAS, operates at the second harmonic of the cyclotron frequency and delivers radiation with a power of 100 W and frequency of 0.26 THz. It is characterized by the high stability of these output parameters during operating periods (up to 12 h). This radiation source has been used with one of the NMR spectrometers at the Institute of Biophysical Chemistry of Goethe University (Frankfurt-am-Main, Germany) [65–67,76]. DNP enhancement of −29 was obtained for an aqueous solution of Fremy's salt. For comparison, in previous experiments, using a solid-state microwave source with a maximum output power of 45 mW, the highest value was −10. These experimentally observed DNP enhancements, which are above the predicted values extrapolated from low-field DNP experiments, demonstrate that DNP is possible in the liquid state even at high magnetic fields.

The design of a modular gyrotron for DNP-enhanced solid-state NMR spectroscopy at 400 MHz (1 H) has been reported in [68]. Its construction allows changing only some elements such as the cavity-uptaper system in order to adapt to the wide range of NMR spectrometers existing at EPFL. This low-power (10–50 W) high-frequency gyrotron (265–530 GHz) is based on a 9.7 T helium-free SCM. Then, the detailed investigation of a modular 260 GHz, frequency-tunable gyrotron equipped with a matching optics unit demonstrated full polarization control of the rf-wave [71]. Furthermore, it has been shown that with a triode MIG gun design, it is possible to perform full power modulation for pulse lengths as short as 30 μs with an arbitrary duty cycle.

In a recent study [70], a fast frequency-tunable, amplitude-switchable 260 GHz gyrotron has been used to obtain a DNP frequency profile by a step-wise sweep of the microwave frequency over 500 MHz, at fixed NMR frequency. By sweeping the anode voltage of the gyrotron a frequency modulation at sweep rates up to 14 kHz has been performed, covering a frequency band of electron spin resonance of 100 MHz. It has been shown that frequency modulation is effective in producing a gain in the enhancement of more than 60% from 15 K to 100 K.

An advanced concept, albeit not yet fully realized, is to integrate (embed) the gyrotron with a single cryomagnet of the spectrometer in such a way as to significantly simplify the whole system and decrease its price. Such a gyrotron called "gyrotrino" has many peculiarities [77–80]. For example, it should operate at extremely low voltage (less than 2 kV), which makes it difficult to form a high-quality electron beam with a sufficient pitch factor and collect it in a low magnetic field. Additionally, the limited space for the resonant cavity dictates to use of diffraction output of the radiation from the cathode end of the cavity. The extensive numerical experiments show that the development of such a gyrotron is feasible despite the technical difficulties and is an appealing alternative to the conventional gyrotrons with a stand-alone magnet used in the existing DNP-NMR spectrometers.

5. XDMR Spectroscopy

X-ray detected magnetic resonance (XDMR) spectroscopy is a pump and probe technique that uses X-ray magnetic circular dichroism (XMCD) to probe the resonant precession of spin or orbital magnetization components pumped by the magnetic field of a strong microwave generated by a sub-THz gyrotron [81,82]. The schematic of the used setup is shown in Figure 5. This method is element and edge-selective and can be used for detailed studies of the precession dynamics of orbital and spin magnetization components.

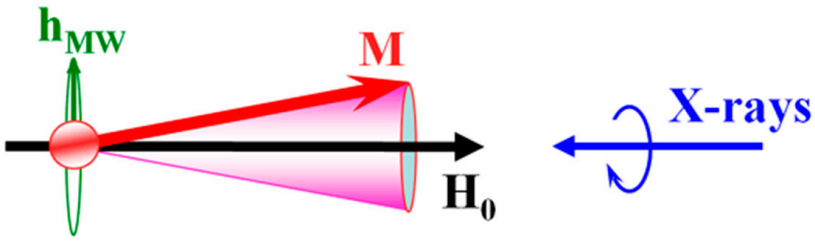

Figure 5. Setup of the XDMR experiments (h_{MW}—magnetic field of the microwave radiation, H_0—bias static magnetic field, M—processing magnetic vector).

The feasibility of this novel spectroscopic technique has been proven in the experiments carried out at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, where an optimized version of the FU II gyrotron build in FIR UF has been installed [82]. This tube generates radiation in a wide frequency range from 70 to 402 GHz (at fundamental or second harmonic resonances) and is capable of delivering high output intensities with peak powers on the order of 1 kW. Operating the gyrotron at short pulses with a duration of 100 μs and a repetition rate of 5 Hz the output power was 5.4 kW in the TE011 mode and 0.9 kW in the TE161 mode. The XDMR spectrometer that uses the gyrotron FU II as a high-power pumping source is installed at the beamline ID12 covers the whole energy range of 2–20 keV and is entirely dedicated to X-ray circular or linear dichroism studies. ESRF is equipped with three helical undulator sources that can deliver very high fluxes of circularly polarized X-ray photons [82]. The gyrotron has been controlled remotely when the X-ray beam is switched on. The first XDMR experiments have been carried out at 76 and 138 GHz operating the gyrotron at the fundamental resonances of the TE_{011} and TE_{021} modes, respectively. The static (bias) magnetic bias field with an intensity $\leq$6 T and oriented parallel to the wavevector of the X-ray radiation has been produced by a split-coil cryomagnet. In order to protect the gyrotron from the stray radiation of the cryomagnet, it is placed far enough (at a distance ca 4 m) and its radiation is delivered to the spectrometer by a quasi-optical transmission line.

The studied materials include YIG or gadolinium-doped YIG films deposited on GGG (gadolinium gallium garnet) substrates that are important for the spintronics.

The researchers who conducted the first gyrotron-based XDMR experiments [81] have stressed that that "this technique is a unique tool to probe the precession dynamics of orbital magnetization components at a precession time scale that is considerably shorter than the duration of the relativistic electron bunches in the ESRF storage ring. So-far, there is no other example of such ultrafast process probed". It is expected that the recent progress in the development of high-performance powerful gyrotrons with increased stability of the output parameters would facilitate further the mastering of this advanced spectroscopy. Furthermore, the results of the experiments suggest some possibilities for further development of this promising novel spectroscopic technique for studying magnetization dynamics and spin transport in a variety of magnetic materials and spintronic devices. It is expected, for instance, that extending the measurements to frequencies of up to 140 GHz will allow to investigate the dynamics of the Van Vleck orbital paramagnetism, to detect the high-frequency normal modes associated with magnetically coupled sub lattices, etc.

6. Measuring of the HFS of Positronium

Positronium (Ps) is the lightest hydrogen-like exotic atom, which is a metastable bound state of an electron and a positron. Its simple structure allows an exact theoretical description of its energy levels and is therefore an excellent object to experimentally test quantum electrodynamics (QED). This leptonic particle–antiparticle system can exist in two states, namely ortho-positronium (o-Ps) and para-positronium (p-Ps). The hyperfine splitting (HFS) between the energy levels of o-Ps and p-Ps is about 203.4 GHz. Using indirect methods (such as measuring the Zeeman splitting in a static magnetic field, which is subject to unavoidable systematic errors), there is a significant discrepancy between the measured HFS values and the theoretical prediction of QED. In an attempt to eliminate these errors, a new method for the direct and accurate evaluation of HFS has been developed [83–86]. In contrast to indirect measurements, the new approach is based on a stimulated transition between o-Ps and p-Ps states induced by irradiation with a strong electromagnetic wave generated by a frequency-tunable gyrotron with a central frequency of about 203 GHz. The experimental setup is shown schematically in Figure 6. The gyrotron radiation is delivered and coupled to a high-finesse Fabry–Pérot cavity in which a power of about 10 kW is accumulated. The experimental setup includes also a gas chamber, a source of positrons, a set of detectors, and an electronic control system. The positronium is produced in the cavity using a ^{22}Na source of positrons and nitrogen mixed with iso-butane as a stopping target. Under the irradiation by an electromagnetic wave with a frequency of about 203 GHz, some of the o-Ps (decaying into three photons) transit into p-Ps (decaying into two photons), and the ratio of two-photon events increases. This process is registered with photon detectors (LaBr3(Ce) scintillators) that are located around the cavity. During the measurements, the gyrotron frequency is varied within an interval of approximately 2 GHz in order to observe a Bret–Wigner resonance of the transition. For the first time, the whole Breit–Wigner resonance of the transition from o-Ps to p-Ps has been measured by tuning the gyrotron in a very wide range from 201 to 205 GHz by changing successively several gyrotron cavities of different radii. In the experiments, the hyperfine transition has been observed with a significance of 5.4 standard deviations. The transition probability that has been measured directly for the first time is found to be $A = 3.69 \pm^{0.48}_{0.29} \times 10^{-8}$ s^{-1}, which is in good agreement with the theoretical value of 3.37×10^{-8} s^{-1} [86].

Remarkably, experiments in fundamental particle physics are usually associated with large experimental infrastructures that include huge machines such as linear accelerators, synchrotrons, colliders, storage rings, bulky detectors, etc. For example, the Large Hadron Collider (LHC) at CERN (the European Organization for Nuclear Research) uses a tunnel with a circumference of 27 km. In contrast to such spacious facilities, the above-mentioned experiments use a table-top setup (see Figure 7) that occupy several square meters only [87].

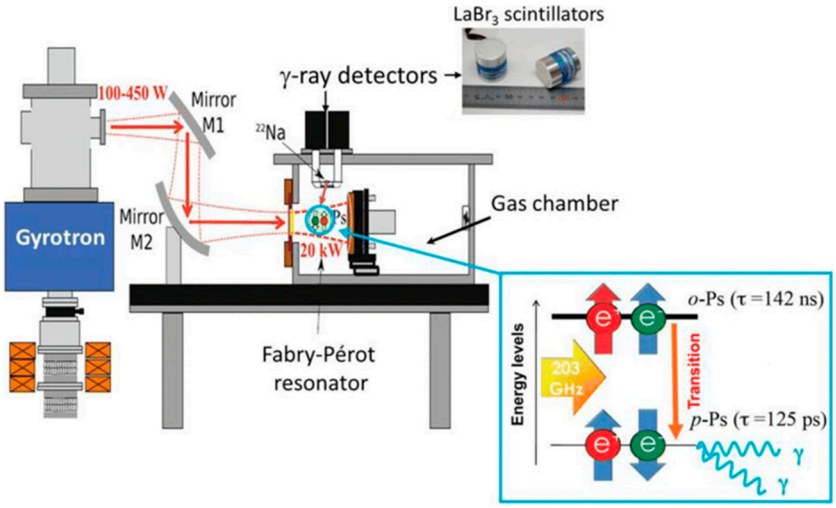

Figure 6. Schematics of the experimental setup.

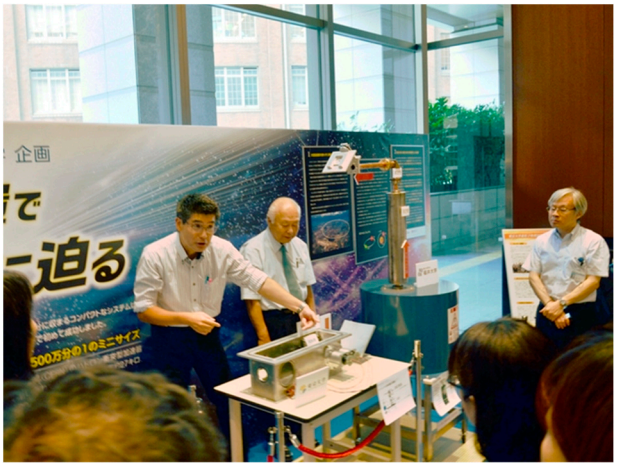

Figure 7. Demonstration of a table-top experiment by Prof. S. Asai (University of Tokyo) and Prof. T. Idehara (University of Fukui) in October 2016.

7. Conclusions and Outlook

The development and application of gyrotrons to various spectroscopic systems are interrelated areas of research that cross-fertilize and create broader links between seemingly distant fields of science and technology. We believe that this trend will be accelerated further by accumulated experience and advances in the theory and practice of computer-aided design of specialized high-performance gyrotrons. This development will also benefit many other applications of gyrotrons, which are used as radiation sources for plasma heating, materials processing, sensing, imaging, driving microwave undulators, accelerating structures, etc., to name a few.

We envisage the following major directions for the development of high-performance gyrotrons for spectroscopy and other applications: (i) further improvement of the methods and systems for precise control and stabilization of the output parameters and frequency control (tunability and modulation); (ii) advancement toward higher frequencies through operation at higher harmonics and using advanced concepts such as LOG (large orbit gyrotron), multi-beam gyrotrons, gyrotrons with complex resonant cavities, etc.; (iii) design and manufacturing of efficient output windows and transmission lines for coupling the gyrotron radiation to the spectrometer.

We believe that the advanced gyrotron-based spectroscopic techniques and systems presented in this review will be continuously improved, optimized, and automated and

will spread to a broader scientific community. We also expect that new, as yet unknown spectroscopic applications will emerge alongside existing methods.

Author Contributions: Both authors contributed equally to the paper. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding. Mentioned IAP RAS data obtained within framework # 0030-20XX-0001.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data that support the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments: We are grateful to the colleagues at IAP RAS, IE BAS, and FIR UF for providing us with information about the recent results of the development and application of gyrotron-based spectroscopic techniques and systems. We also acknowledge the great contribution of the late Professor Toshitaka Idehara—our supervisor as a founder and the first director of the Research Center for Development of Far-Infrared Region University of Fukui, friend, and collaborator, in the development of the scientific field to which this paper is devoted.

Conflicts of Interest: The authors declare no conflict of interest.

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