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Detection of electron paramagnetic resonance absorption using frequency modulation

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Abstract

A frequency modulation (FM) method was developed to measure electron paramagnetic resonance (EPR) absorption. The first-derivative spectrum of 1,1-diphenyl-2-picrylhydrazyl (DPPH) powder was measured with this FM method. Frequency modulation of up to 1.6 MHz (peak-to-peak) was achieved at a microwave carrier frequency of 1.1 GHz. This corresponds to a magnetic field modulation of 57 μT (peak-to-peak) at 40.3 mT. By using a tunable microwave resonator and automatic control systems, we achieved a practical continuous-wave (CW) EPR spectrometer that incorporates the FM method. In the present experiments, the EPR signal intensity was proportional to the magnitude of frequency modulation. The background signal at the modulation frequency (1 kHz) for EPR detection was also proportional to the magnitude of frequency modulation. An automatic matching control (AMC) system reduced the amplitude of noise in microwave detection and improved the baseline stability. Distortion of the spectral lineshape was seen when the spectrometer settings were not appropriate, e.g., with a lack of the open-loop gain in automatic tuning control (ATC). FM is an alternative to field modulation when the side-effect of field modulation is detrimental for EPR detection. The present spectroscopic technique based on the FM scheme is useful for measuring the first derivative with respect to the microwave frequency in investigations of electron-spin-related phenomena.

Keywords: Phase-sensitive detection; Frequency modulation; Automatic tuning control; Automatic matching control; Electronically tunable resonator

1. Introduction

Continuous-wave (CW) electron paramagnetic resonance (EPR) spectroscopy is a magnetic resonance (MR) technique for detecting unpaired electrons, and has been used for free-radical-related studies in analytical chemistry and biomedical applications [1–4]. Since the relaxation time of an electron spin system is extremely short compared to that of a nuclear spin system, such as in proton nuclear magnetic resonance, most EPR spectroscopy uses CW instead of a pulse protocol. To make highly sensitive detection possible, magnetic field modulation and phase-sensitive detection (PSD) have been used in CW-EPR spectroscopy, which has been a basic technology in EPR spectroscopy [5]. Magnetic field modulation makes it possible to record the first-derivative EPR absorption as a function of the magnetic field. Since EPR absorption is essentially a function of the microwave frequency, the first-derivative display of EPR absorption can be obtained as a function of the microwave frequency instead of the magnetic field. The frequency modulation (FM) method was investigated theoretically in the 1950s and compared with the field modulation scheme [6–11]. In principle, however, magnetic field modulation differs from frequency modulation [12,13]. Spectroscopic techniques using the FM scheme could be useful for measuring the first derivative with respect to the microwave frequency in investigations of electron-spin-related phenomena.

Thus far, magnetic resonance techniques have been reported to detect unpaired electrons without using magnetic field modulation, e.g., time-resolved EPR spectroscopy [14,15], multiquantum EPR spectroscopy

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[16], longitudinally detected EPR spectroscopy [17,18], microwave amplitude modulation [19], and proton–electron double resonance imaging, also known as Overhauser enhanced magnetic resonance imaging [20,21]. These are advanced methods in EPR instrumentation that require specific microwave technologies for the spectrometer setup. There are also non-inductive methods for detecting electron spins, e.g., the force detection method [22] and electron-spin-resonance-scanning tunneling microscopy [23].

The most hazardous side-effect of magnetic field modulation is the mechanical vibration due to $\mathbf{I} \times \mathbf{B}$, where **I** is the current and **B** is the static magnetic field. Two kinds of current, i.e., the conducting current in a modulation coil and the eddy current induced by the time-varying magnetic field in metal media such as a microwave resonator, are involved in this mechanical vibration. To perform PSD for EPR detection, a time-varying magnetic field is generated by the conducting current in the modulation coil, and this perturbs the static magnetic field. This side-effect becomes the major problem in high-field EPR spectroscopy and CW-NMR spectroscopy with a multi-Tesla magnet. This problem can be solved if magnetic field modulation is not used in CW-EPR spectroscopy. In this context, the FM scheme is a CW method for avoiding mechanical vibration due to $\mathbf{I} \times \mathbf{B}$. Recently, we reported preliminary results in 1.1 GHz CW-EPR spectroscopy with the FM method [24]. However, we did not resolve key technical issues: (i) baseline stability, (ii) lack of modulation amplitude, and (iii) violation of the 'transfer of modulation' principle. Microwave amplitude and frequency modulation were at one time considered for detecting unpaired electrons in EPR spectroscopy. However, Hyde and coworkers [25] raised an important point, i.e., "they violate the 'transfer of modulation' principle: namely, that modulation should be transferred to the microwave carrier only when magnetic resonance occurs." This point should be remembered when we consider the behavior of a CW-EPR spectrometer using frequency modulation.

The background signal in EPR detection with the FM method is mainly due to the frequency characteristics of the microwave elements, the impedance matching network and the tuning circuit in a microwave resonator. Thus, engineering outcomes are crucial in a CW-EPR spectrometer with the FM method. In the conventional field modulation scheme used in CW-EPR spectroscopy, the envelope of the microwaves reflected at the resonator does not contain the signal at the modulation frequency of field modulation in the absence of EPR absorption. However, the amplitude-modulated microwaves due to field modulation will be reflected upon EPR absorption, and energy dissipation occurs in the resonator. In contrast, the microwaves reflected at the resonator are influenced by the frequency characteristics of the microwave elements, which overlap EPR absorption in the FM method. This violates the 'transfer of modulation' principle. Thus, the magnitude of the detected microwaves is modulated at the modulation frequency in the FM method, even if there is no EPR absorption.

In this report, we demonstrate that the FM method in 1.1 GHz CW-EPR spectroscopy gives good stability and practical performance, while violation of the 'transfer of modulation' principle is inherent in the FM scheme. The baseline stability was significantly improved by automatic tuning control (ATC) and automatic matching control (AMC), also known as automatic coupling control [26,27]. These control techniques enable more stable operation of the EPR spectrometer, and allow for the application of a larger modulation amplitude to detect first-derivative absorption.

2. Methods

2.1. Spectrometer setup

We used a standard reflection scheme for an EPR microwave bridge in a 1.1-GHz EPR spectrometer during FM detection. Fig. 1 shows a diagram of the spectrometer setup with the FM scheme. After envelope detection in the microwave bridge, the detected signal was amplified by amplifier No. 1, which has a bandwidth of 0.2–4 kHz. PSD was then performed with a lock-in amplifier (NF Electronic Instruments, Japan, 5610B) to record EPR absorption in the first-derivative mode. The modulation signal at 1 kHz, which was generated with a function generator (Agilent Technologies, CA, 33120A), was also used as a reference signal for the lock-in amplifier.

The microwave frequency is modulated to detect the EPR absorption curve. If the resonance frequency of a microwave resonator is independent of the modulation for the EPR detection scheme, the microwaves are significantly reflected at the resonator. To avoid significant reflection, a resonator with a low-quality factor should be used. However, a low-quality factor is detrimental for highly sensitive EPR spectroscopy. The influence of the quality factor on the signal-to-noise ratio in CW-EPR spectroscopy has been well documented [28]. To solve this problem, we have to adjust the resonance frequency and the impedance matching of the resonator in the FM method. Thus, we used an electronically tunable surface-coil-type resonator operating at 1.1 GHz and the ATC and AMC systems, simultaneously [29,30]. The resonance frequency of the resonator is automatically adjusted to the microwave frequency by the ATC system in our experiments. Table 1 lists the typical parameters in our spectrometer setup and automatic control systems.

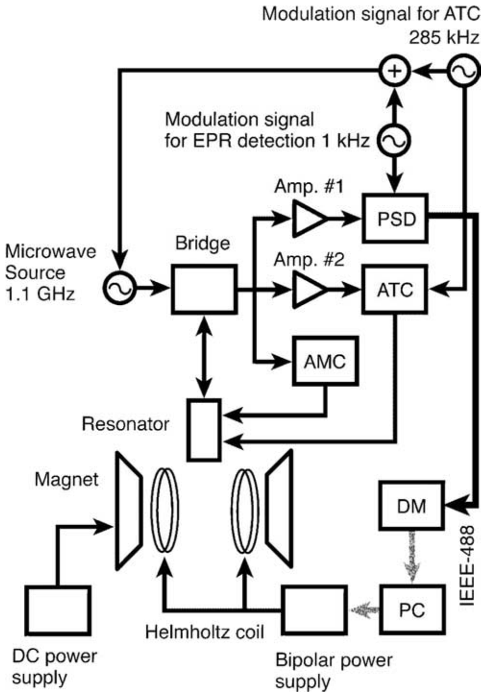

Fig. 1. Diagram of a continuous-wave EPR spectrometer that incorporates a frequency modulation method. A microwave synthesizer (Anritsu, Japan, MG3633A) is used as a microwave source and the voltage applied to the electronic tuning port controls the microwave frequency. A 1.1-GHz electronically tunable resonator is used in the spectrometer [29,30]. The automatic tuning control (ATC) system allows the tunable resonator to follow the microwave frequency modulated with a 1 kHz signal. After RF detection and amplification, the EPR signal is detected by a phase-sensitive lock-in amplifier (PSD) (NF Electronic Instruments, Japan, 5610B) associated with a reference signal from a signal synthesizer (Agilent Technologies, CA, 33120A). The analog-output voltage of the lock-in amplifier is recorded with a digital multimeter (DM) (Agilent Technologies, CA, 34401A) and the data stored in the multimeter are transferred to a personal computer (PC) through an IEEE-488 interface bus. The automatic matching control (AMC) system maintains good impedance matching between the transmission line and the resonator. A bipolar DC power supply (Kikusui Electronics, Japan, PBX20-5) drives the Helmholtz coil for field scanning, and the maximum magnetic flux density for field scanning is ±4.5 mT. Data acquisition in EPR spectra is carried using a LabVIEW-based control program on a personal computer. In the actual experimental setup, the resonator is placed between the pole caps of a resistive magnet and the Helmholtz coil, while the resonator is apart from the magnet in the diagram.

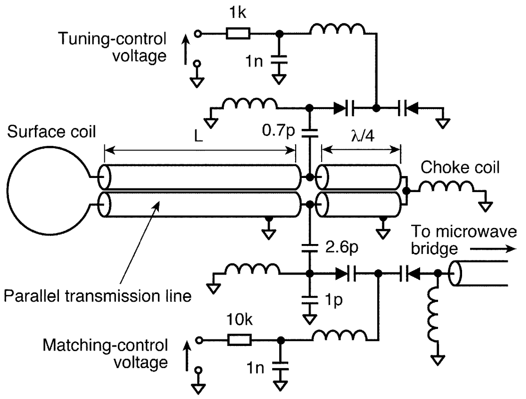

Fig. 2. Schematic diagram of a 1.1-GHz electronically tunable surface-coil-type resonator. The single-turn coil called a surface coil (10 mm in diameter) is connected to the parallel transmission line formed by a 50-Ω semi-rigid coaxial cable (5 mm in diameter). A surface coil was made by copper wire 1 mm in diameter, and the length of the transmission line L in the resonator used in our experiments was 102 mm. Two kinds of control circuits are added to the parallel transmission line, i.e., the tuning circuit and the matching network that involve varactor diodes. The capacitance of the varactors used (Toshiba, Japan, 1SV186) can be adjusted from 0.7 to 4.0 pF. The resonance frequency and the quality factor of the resonator used are 1124 MHz and 260, respectively.

2.2. Electronically tunable resonator

The resonance frequency and the input impedance of the tunable resonator can be controlled, since the tuning circuit and the matching network involve varactor diodes. Fig. 2 shows a schematic diagram of a 1.1-GHz electronically tunable surface-coil-type resonator. While this type of resonator has already been reported elsewhere [29], we improved this tunable resonator especially for EPR spectroscopy with the FM method. This tunable resonator consists of a single-turn loop (10 mm in diameter) and a parallel transmission line that is formed by a 50-Ω semi-rigid coaxial line (5 mm in diameter). The resonance frequency of the resonator mainly depends on the length of the transmission line and the inductance of the single-turn loop called a surface coil. Two additional circuits are connected to the parallel transmission line, as shown in Fig. 2. One is the tuning circuit to control the resonance frequency, and the other is the matching network to adjust the input impedance of the resonator to the

Table 1
Typical parameters of EPR detection, automatic tuning control (ATC), and automatic matching control (AMC) in the experiments

	EPR detection	ATC	AMC
Modulation frequency	1 kHz	285 kHz	
Frequency deviation	25 kHz–1.6 MHz (peak-to-peak)	56 kHz (zero-to-peak)	
System bandwidth		96 kHz	10 Hz
Open-loop gain at the low-frequency band		172	76
Incident microwave power	6.3 dBm		
Quality factor	260		

characteristic impedance of the coaxial cable connected to the microwave bridge. By applying reverse-bias potentials to the varactors (Toshiba, Japan, 1SV186), the capacitance of the varactors can be varied and the circuit parameters can be controlled remotely. A 6-mm-thick copper shielding case contains the half-wave line and additional circuits to avoid unnecessary interference.

The experimental results confirmed that there is no significant additional noise in EPR spectra measured with the tunable resonator [29]. Additional noise due to the varactors is an important technical issue for making the spectrometer highly sensitive. The resonance frequency of the tunable resonator can be controlled in the range of ±6 MHz with a coefficient of 1.26 MHz/V. The cut-off frequencies of the RC circuits in the control ports were adjusted to make the response of the tunable resonator suitably fast.

2.3. Automatic tuning control

The development of automatic control systems is a key technical issue in achieving the practical performance of a spectrometer with the FM method. The reference for the feedback loop in ATC is the microwave frequency, and the resonance frequency of the resonator is automatically tuned to the microwave frequency [27]. In ATC, the microwave carrier is modulated through the frequency modulation mode at 285 kHz, and PSD was performed at the same modulation frequency to detect the difference between the microwave carrier and the resonance frequency.

The ATC system is based on PSD, which is similar to a conventional automatic frequency control (AFC) system in a CW-EPR spectrometer. Fig. 3 shows the circuit diagram of ATC and AMC used in our experiments. After envelope detection with a negative-peak detector, the output of the detector was amplified with a non-inverted amplifier No. 2 (Analog Devices, MA, AD745) with a bandwidth of 80 kHz to 2 MHz. An inverted amplifier (Analog Devices, MA, OP 37) then amplified the signal again. The output of the inverted amplifier was delivered to the RF port of a double-balanced mixer (Mini-Circuits, NY, GRA-6H). A resistor-tunable oscillator (NF Electronic Instruments, Japan, CG-202R3) outputs the signal of 285 kHz, which is used for the modulation signal and the reference signal for PSD in the ATC system. This signal is sent to the LO port of the double-balanced mixer. The output of the IF port in the double-balanced mixer is a product of the RF and LO signals, and is integrated with an integrator made by an operational amplifier (Analog Devices, MA, OP77). The output of the integrator is connected to a low-pass filter. This output voltage is shifted by a summing amplifier and applied to the tuning-control port.

The ATC system in our spectrometer has a system bandwidth of 96 kHz when the frequency deviation is

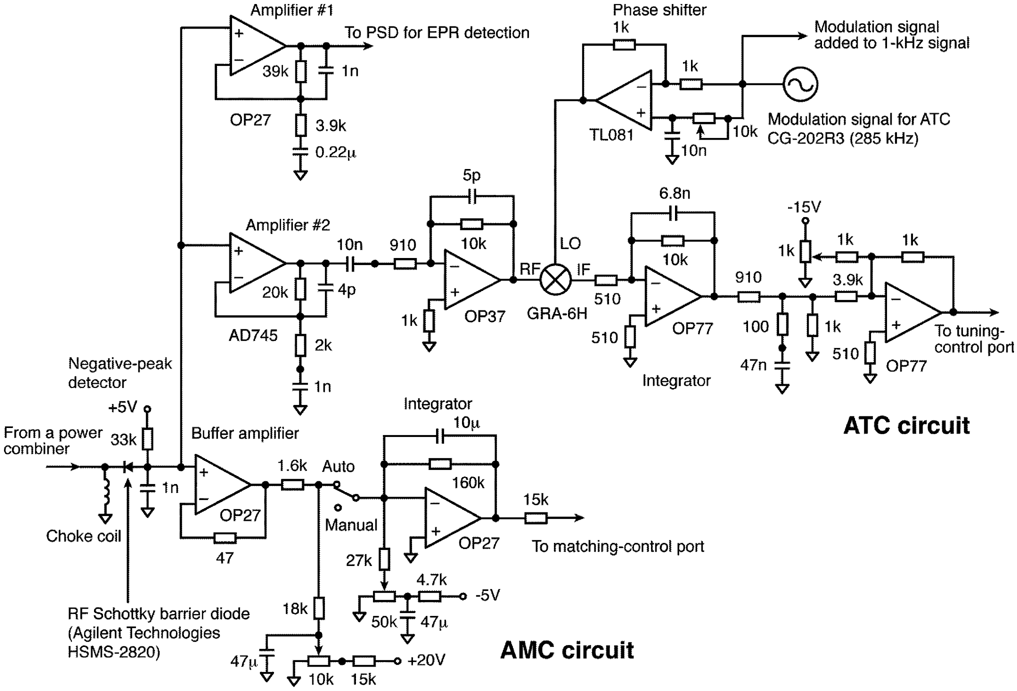

Fig. 3. Circuit diagram of the automatic tuning control (ATC) and automatic matching control (AMC) systems. The ATC system is based on the phase-sensitive detection (PSD) scheme. The output of the ATC circuit is fed back to the tuning-control port of the tunable resonator shown in Fig. 2. The AMC system uses the DC detection scheme. The voltage adjusted by a potentiometer (10 kΩ) reduces the output of the buffer amplifier (Analog Devices, MA, OP27) to zero in the absence of microwaves reflected at the resonator. The integrator made by an operational amplifier (Analog Devices, MA, OP27) integrates a shift in the output voltage of the detector, and is fed back to the matching-control port of the resonator.

56 kHz (zero-to-peak) and the incident microwave power is 6.3 dBm. The characteristics of the ATC system can be estimated by linear control theory [31]. For frequency modulation at 1 kHz, the ATC system tunes the resonance frequency of the tunable resonator with a delay of 0.3°, which means that the ATC system is fast enough to adjust the resonance frequency to the modulated microwave frequency in the FM method.

2.4. Automatic matching control

The AMC system is based on a DC-detection scheme. The input impedance of the resonator affects the phase and amplitude of the microwaves reflected at the resonator. If the phase and amplitude of the reflected microwaves are monitored, one can sense the degree of impedance matching between the resonator and the coaxial cable connected to the microwave bridge. The microwaves coming from the reference arm are combined with those reflected from the resonator before envelope detection. Thus, the phase and amplitude of the reflected microwaves affect the output voltage of the negative-peak detector. Thus, one can monitor the degree of impedance matching of the resonator by measuring the output voltage of the negative-peak detector. The AMC system maintains well-defined impedance matching between the resonator and the coaxial line to improve the baseline stability. While slow perturbation such as a shift in temperature should be compensated to make the baseline stable, the reflected microwaves perturbed by the modulation frequency (1 kHz) for EPR detection should not be compensated. We chose the system bandwidth of AMC to be 10 Hz, so that the AMC circuit would satisfy the requirement for the characteristics in the frequency domain.

The reference of the feedback loop of the AMC system is the DC voltage of the negative-peak detector in the absence of microwaves reflected at the resonator. The AMC circuit shown in Fig. 3 was based on a previously reported circuit diagram [29], but the circuit parameters were adjusted to the required system bandwidth mentioned above. The difference voltage between the reference voltage and the output voltage of the detector was integrated with an integrator made by an operational amplifier (Analog Devices, MA, OP27). The integrated voltage was fed back to the tunable resonator to adjust the input impedance of the resonator. To establish a negative feedback loop for AMC, we adjusted the line length between the resonator and the microwave bridge, since the phase of the reflected microwaves depends on this length.

2.5. Data acquisition and EPR measurements

A magnetic field sweep was used to record EPR spectra in the present FM method. A resistive magnet was used to generate the static magnetic field B_0, and a Helmholtz coil (100 mm in diameter) was used for the field sweep. The Helmholtz coil for the field sweep was driven by a programmable bipolar DC power supply (Kikusui Electronics, Japan, PBX20-5), and the maximum magnetic flux density for field scanning was ±4.5 mT. The field sweep and data acquisition for EPR detection were controlled by a LabVIEW-based program and an IEEE-488 interface bus. The analog-output voltage of the lock-in amplifier used for EPR detection was recorded with a digital multimeter (Agilent Technologies, CA, 34401A). The data stored in the multimeter were transferred to a personal computer through the IEEE-488 interface bus.

An increase in the magnitude of modulation (frequency deviation) is a critical issue for making the FM method practical. The frequency deviations were changed from 25 kHz to 1.6 MHz (peak-to-peak), which correspond to a magnetic field modulation of 0.9–57 μT (peak-to-peak) at a static magnetic field of 40.3 mT. The available frequency deviation in the microwave source used (Anritsu, Japan, MG3633A) was limited to below 3.2 MHz (peak-to-peak) at a microwave frequency of 1.1 GHz. Thus, the frequency deviation for detecting the first-derivative EPR absorption was limited within this range. In our measurements, the EPR sample consisted of 20 mg of 1,1-diphenyl-2-picrylhydrazyl (DPPH) powder in a disposable polypropylene test tube (1.5 ml).

3. Results

3.1. EPR signal intensity as a function of frequency deviation

The signal intensities of the first-derivative EPR spectra in Fig. 4 were proportional to the frequency deviation in the FM method. The signal intensity in EPR spectra is proportional to the modulation magnitude, i.e., the frequency deviation, if the modulation amplitude is within the intrinsic linewidth of EPR absorption, and there is no saturation in EPR measurements. The EPR linewidth of DPPH power was 90 μT in the signal recorded at a frequency deviation of 200 kHz in Fig. 4. The linewidth of other signals in Fig. 4 was almost similar to that detected at a frequency deviation of 200 kHz. While the baseline in the top signal in Fig. 4 was slightly less stable than others with smaller frequency deviations, these baselines were reasonably stable.

3.2. Background signals

A shift in the voltage for controlling the impedance matching makes the detected signals noisier, as shown in Fig. 5a. The AMC system automatically adjusted the

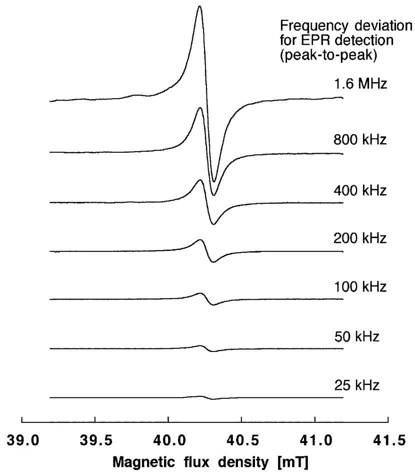

Fig. 4. EPR spectra recorded using frequency modulation (FM). The microwave carrier frequency was 1124 MHz, and was modulated at 1 kHz for phase-sensitive detection (PSD). The sample was 20 mg of 1,1-diphenyl-2-picrylhydrazyl (DPPH) powder. The frequency deviation was 56 kHz (zero-to-peak) for automatic tuning control (ATC) to tune the resonance frequency of the resonator to the modulated microwave frequency. In all measurements, the incident microwave power was 6.3 dBm, the scan time was 30 s, the time constant of the lock-in amplifier was 30 ms, and the scan width was 2.0 mT. The efficiency for generating RF magnetic field was 77 μT/W$^{1/2}$ for the tunable resonator used in the experiments.

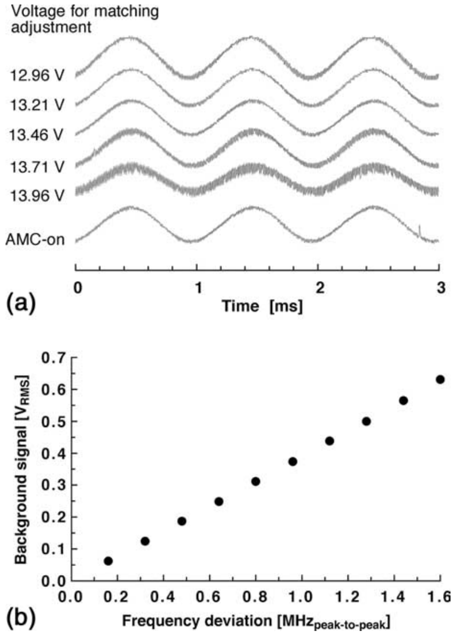

Fig. 5. (a) Background signals for phase-sensitive detection in the FM method. The root-mean-square voltage of the bottom trace is approximately 80 mV$_{RMS}$, and other signals are also displayed in the same scale. Even with no EPR absorption, there is output from the modulation signal, called the background signal. (b) The root-mean-square voltage of the background signal as a function of the frequency deviation. In this measurement, the frequency deviation for ATC was 56 kHz (zero-to-peak) without a static magnetic field.

reverse-bias potential to a voltage that maintained good impedance matching (13.46 V), which may reduce the noise level of the detected signals. Since the FM method in CW-EPR spectroscopy violates the 'transfer of modulation' principle, the background signal at the modulation frequency (1 kHz) was observed after RF detection. The background signal depends on the impedance matching of the resonator. Fig. 5a shows the output signals of amplifier No. 1 in Fig. 3 when the frequency deviation for PSD in EPR detection was 200 kHz (peak-to-peak) and the frequency deviation for PSD in the ATC systems was 56 kHz (zero-to-peak). When good impedance matching remained at 13.46 V, the higher-frequency signals superimposed on the signal at 1 kHz reached a minimal amplitude. These higher-frequency components in the background signals mainly contribute to the signals at 285 and 570 kHz. Since the modulation signal at 285 kHz was used for ATC, the detected signals included the first and second harmonics.

Upon the application of a larger modulation signal, we found significant background signals. Fig. 5b shows the amplitude of the background signals as a function of the frequency deviation for EPR detection. The frequency deviation for ATC was 56 kHz (zero-to-peak), and AMC was applied in all measurements. In Fig. 5b, the amplitudes of the background signals were proportional to the frequency deviation for EPR detection. These results mean that the spectrometer functions as a frequency discriminator because of the frequency characteristics of the microwave elements.

3.3. Lineshape distortion in EPR spectra

The phase delay and a lack of the open-loop gain of ATC affect the lineshape. As stated above, the ATC system tunes the resonance frequency of the resonator to the

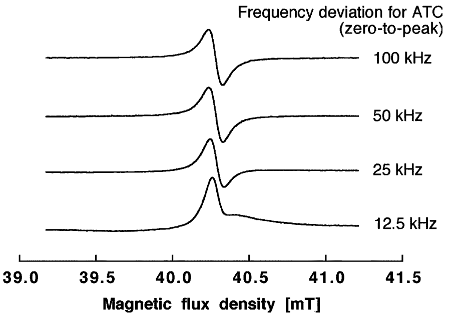

Fig. 6. Effect of the frequency deviation for automatic frequency control (ATC) on the lineshape of the first-derivative EPR absorption of DPPH powder. The frequency deviation for EPR detection was 200 kHz (peak-to-peak) and the experimental settings were the same as in Fig. 4. The lineshape was distorted when the frequency deviation for ATC was decreased. This suggests that the phase delay and a lack of the open-loop gain of the ATC system lead to spectral distortion. The open-loop gain of ATC depends on the frequency deviation, the quality factor of the resonator, and the incident microwave power.

modulated microwave frequency in the FM method. Fig. 6 shows the EPR spectra of DPPH powder when the frequency deviation for EPR detection was 200 kHz (peak-to-peak). The lineshape was distorted when the frequency deviation for ATC was decreased. The experimental findings strongly suggest that an appropriate set of control characteristics for ATC is necessary to avoid significant distortion of first-derivative absorption. The open-loop gain and the phase delay of ATC depend on the parameters of the spectrometer setup, i.e., the frequency deviation, the quality factor of the resonator and the incident microwave power. If the frequency deviation for the modulation signal at 285 kHz is large enough to adjust the resonance frequency to the modulated microwave frequency, one can record the first-derivative absorption with a less distorted lineshape.

4. Discussion

We applied a frequency deviation of 1.6 MHz (peak-to-peak) in the FM method. This corresponds to a magnetic field modulation of 57 μT (peak-to-peak) at 40.3 mT. One of our objectives was to increase the magnitude of modulation in the FM method, i.e., the frequency deviation for EPR detection. Although the modulation is still smaller than the linewidth of DPPH powder, we dramatically improved the capability of the FM method. The frequency deviation for EPR detection in our previous report [24] was only 28 kHz (peak-to-peak), which corresponds to 1 μT in field modulation. Since we had better baseline stability than without AMC in our spectrometer, we were able to apply a larger frequency deviation for EPR detection. AMC is a key technical advantage in the present study.

We obtained reasonable performance for a 1.1-GHz CW-EPR spectrometer with the FM method. The weakness of the FM method is that it violates the 'transfer of modulation' principle. This may explain the poor results with previous attempts at EPR spectroscopy using the FM method. Theoretical investigations of the FM method have been reported [9–13]. However, instrumentation for the FM method has been difficult to achieve without the use of a tunable microwave resonator and automatic control systems. A theoretical investigation [13] predicted a difference between the lineshape in magnetic field modulation and that in the FM method. Nevertheless, when a small frequency modulation and magnetic field sweep are used, the difference between EPR absorptions recorded by field and frequency modulation becomes ultimately small. The resultant EPR absorption spectrum depends not only on spin physics but also on the characteristics of the feedback loops in the spectrometer, as shown in Fig. 6. The relationship between the lineshape and the spectrometer setting requires further investigation and engineering outcomes that can affect the practical performance of EPR spectroscopy with the FM method. A possible solution is to use an automatic gain control technique in the ATC system. This should make the spectrometer more robust, even if the frequency deviation for ATC varies.

In the ATC system, a finite open-loop gain and a phase delay in the modulation frequency give a difference between the resonance frequency and the modulated microwave frequency. This leads to the reflection of microwaves at the resonator. In addition, the frequency characteristics of the microwave elements used in the spectrometer affect the amplitude of the modulated microwaves. After envelope detection, a sinusoidal signal at the modulation frequency is observed, and this is called the background signal. Even if there is no EPR absorption, the signal at the modulation frequency for EPR detection is observed after envelope detection. This is a result of violating the 'transfer of modulation' principle. Quantitative analysis of the background signal is necessary to determine the main reason for this problem for a specific spectrometer setup. Thus, it is important to investigate the characteristics of control systems and microwave circuits to suppress the background signal and lineshape distortion.

EPR spectroscopy with the FM method can solve the problem of mechanical vibration due to $\mathbf{I} \times \mathbf{B}$. The force of $\mathbf{I} \times \mathbf{B}$ is more significant in high-field EPR spectroscopy using a superconducting magnet, e.g., with a magnetic flux density of 8.9 T at 250 GHz [32]. This vibration affects the resonator system in the spectrometer. The FM method can also solve the potential problem of heating in the modulation coils. A shift in the temperature near a resonator system may cause technical problems. The influence of heating on the dimensions of the components in the resonator system can affect the key parameters in an EPR spectrometer, i.e., the resonance frequency and the impedance matching. In particular, this advantage of being able to avoid heating in the modulation coils could be useful in high-field EPR with quasi-optical frequencies.

The technical limitation of frequency deviation in the FM method can be resolved at higher frequencies. This is because the ratio between the frequency deviation corresponding to the linewidth and the microwave carrier frequency becomes small at higher frequencies. If a resonator used in high-field EPR spectroscopy has a large enough bandwidth to change the microwave frequency in the FM method, no significant reflection of the electromagnetic waves will occur at the resonator. In such a circumstance, no automatic control circuits and no tunable resonator are needed to suppress the significant reflection of the electromagnetic waves in the FM scheme. An electronically controllable signal source and a tunable resonator in a high-field EPR spectrometer could be important technical issues when the FM method in high-field EPR spectroscopy requires the use of automatic control systems, as demonstrated in the present article.

The deviation of frequency modulation is generally limited for a microwave source. In the microwave synthesizer used in our experiments, the maximum frequency deviation was 3.2 MHz (peak-to-peak) at a microwave carrier frequency of 1.1 GHz. This ratio is equivalent to 114 μT (peak-to-peak) for a static magnetic field of 40.3 mT in the field modulation scheme. In contrast, a microwave synthesizer (for example, model E8251A from Agilent Technologies) can provide a deviation of 8 MHz (zero-to-peak) at a carrier frequency of 9.5 GHz in frequency modulation. This deviation corresponds to 0.57 mT (peak-to-peak) at 0.34 T in the field modulation scheme. Considering this technical limitation, it is easier to apply a greater magnitude of frequency modulation at higher frequencies, such as X-band. A cavity resonator with a high quality factor has been used in X-band CW-EPR spectroscopy. The bandwidth of such a resonator is not so broad. If the resonator has an electronically tunable function, the narrow bandwidth of the resonator is not a problem in a spectrometer using frequency modulation. This is because the resonance frequency is always adjusted to the modulated microwave frequency with the ATC system.

A potential benefit of the frequency modulation scheme is uniform modulation over the material measured. When the static magnetic field is modulated by a time-varying magnetic field generated by modulation coils, conductive materials that make a resonator can affect the distribution of the time-varying magnetic field due to eddy currents in the resonator. This directly affects the intensity of the EPR spectrum and gives an artifact in EPR imaging in the field modulation scheme. In contrast, the deviation of frequency modulation is essentially uniform over the material measured, even if volume-coil-type resonators such as a loop-gap resonator are used. Such resonators have a major problem regarding the penetration of magnetic field modulation.

In summary, our experimental findings suggest that the FM method with a tunable resonator is an alternative solution to achieve phase-sensitive detection when the side-effects of magnetic field modulation are detrimental for EPR detection. The FM method makes it possible to measure a physical quantity related to the derivative with respect to the frequency in magnetic resonance phenomena. Further investigations of the difference between field and frequency modulation for EPR spectra may reveal a potential benefit of frequency modulation, especially for paramagnetic samples with a longer relaxation time.

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