

Nonequivalent spectra of unpaired electrons in field and frequency modulation

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Abstract

We report a difference in the spectral lineshapes of continuous-wave (CW) electron paramagnetic resonance (EPR) spectroscopy between field and frequency modulation. This finding addresses the long-standing question of the effect of modulation in EPR absorption. We compared the first-derivative EPR spectra at 1.1 GHz for lithium phthalocyanine crystals, which have a single narrow linewidth in the EPR absorption spectrum, using field and frequency modulation. The experimental findings suggest that unpaired electrons have different behaviors under perturbation due to field and frequency modulation.

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1. Introduction

Electron spins play a key role in several scientific fields such as spintronics [1], quantum computing [2], materials science [3], and biomedical studies [4–6]. Electron paramagnetic resonance (EPR) spectroscopy is used to detect unpaired electrons in a sample. Most applications of EPR spectroscopy use a continuous-wave (CW) detection method, since the relaxation time of a spin system is extremely short compared to that of a nuclear spin system. Ever since Zavoisky [7] discovered EPR, it has been unclear whether or not field and frequency modulation are equivalent. Magnetic field modulation is used to detect first-derivative EPR absorption with respect to the magnetic field. Since the EPR phenomenon is also a function of the microwave frequency, a frequency modulation scheme can also be used to obtain the spectrum with respect to the frequency. Time-dependent energy dissipation in a microwave resonator due to modulation leads to the reflection of incident microwaves at the resonator. Amplitude-

modulated microwaves reflected at the resonator are then detected in a CW-EPR spectrometer. If the effect of modulation is considered semiclassically, the two modulation schemes can be considered equivalent [8–10]. In contrast, Zhong and Pilbrow [11] pointed out that field and frequency modulation are not equivalent in CW-EPR spectra. A theoretical investigation of the effect of modulation has recently been reported, and claims that “the field-modulation and the frequency-modulation technique are not equivalent, neither in mathematical formulation nor physically” [12]. Kálin et al. measured the EPR spectra of lithium phthalocyanine (LiPc) crystals under large magnetic field modulation at 1 MHz in order to demonstrate the validity of their theoretical investigations of the modulation-induced sidebands in EPR spectra. They showed that the modulation-induced sidebands are well explained by multiple photon transitions rather than single-photon transition [12]. Nevertheless, no experimental evidence has yet been offered to support a difference between the spectral lineshapes in field and frequency modulation. This is because a spectrometer that uses frequency modulation is not practically used in CW-EPR spectroscopy. In this report, we provide experimental evidence of a difference in

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the spectral lineshapes in the two modulation schemes in CW-EPR spectroscopy. While the frequency modulation scheme is an old idea in EPR studies [13–15], it has not survived in modern EPR spectroscopy. To evaluate the effect of modulation in CW-EPR spectroscopy, we developed a CW-EPR spectroscopy using frequency modulation with automatic control techniques [16,17].

2. Methods

2.1. Concept of the frequency modulation scheme

Before reporting the experimental results, we briefly explain the concept of the field-sweep frequency modulation scheme and the spectrometer setup. Fig. 1A shows the concept of the frequency modulation scheme in CW-EPR spectroscopy. Instead of a field modulation scheme as shown in Fig. 1B, frequency-modulated microwaves are converted into amplitude-modulated microwaves due to impedance mismatching induced by EPR absorption. Thus, we can measure the first-derivative EPR absorption with respect to the microwave frequency in the frequency modulation scheme using phase-sensitive detection (PSD). In the frequency modulation scheme, the resonance frequency of an electronically tunable microwave resonator is synchronized with the modulated microwave frequency. The quality factor of the resonator thus does not affect the spectral lineshapes but does affect the sensitivity of the spectrometer.

2.2. EPR sample

We measured lithium phthalocyanine (LiPc) crystals [18–21], which are oxygen-sensitive and have a narrow EPR linewidth, as an EPR sample with a relatively long relaxation time. In the absence of saturation, the measured sample had an EPR absorption linewidth of $14 \mu\text{T}$ at a microwave frequency of 1.1 GHz (the static magnetic flux density is 40 mT). This linewidth corresponds to 392 kHz in the frequency domain. The LiPc crystals used in our experiments were a generous gift from Dr.

Harold M. Swartz of Dartmouth Medical School, Hanover, NH. The LiPc crystals (1.9 mg) were placed in a capillary tube (1 mm in diameter), which was then evacuated and shielded. The pressure of air in the tube was 2 mmHg when it was shielded. The sample tube was placed at the center of the surface coil of the tunable resonator. All measurements were carried out with these parameters: scan time 20 s, scan width 0.2 mT, time constant of the lock-in amplifier 20 ms, and applied microwave power 4.7 dBm.

2.3. Spectrometer setup

In our 1.1-GHz home-built spectrometer using a frequency modulation scheme, the resonance frequency of a microwave resonator can be adjusted to a modulated microwave frequency with an automatic tuning control (ATC) system. A previously reported spectrometer [17] was modified to make higher modulation frequencies accessible. Very rapid automatic control of the resonance frequency is not an easy task. Thus, we used an open-loop frequency control system combined with ATC to adjust the resonance frequency of the resonator to the modulated microwave frequency. An automatic matching control (AMC) system, also known as automatic coupling control, can maintain good impedance matching in the low-frequency band up to several kilohertz [22–27]. One of the key advantages in our spectrometer is automatic control technology to make the frequency modulation scheme possible. For the signal induced at a specific frequency, highly sensitive detection is possible with a phase-sensitive lock-in amplifier. Thus, we can record only the signal at the modulation frequency for EPR detection. This is how artifact signals are suppressed.

We used a standard reflection scheme for an EPR microwave bridge in a 1.1-GHz EPR spectrometer. The development of a spectrometer using frequency modulation has been reported elsewhere [17]. In this study, we needed to apply high modulation frequencies to an EPR sample, LiPc crystals. A diagram of the modified spectrometer setup is shown in Fig. 2. A microwave signal generator (Agilent Technologies E8251A, CA) sent signals to the microwave bridge. After envelope detection in the microwave bridge, the detected signal was amplified by amplifier #1, which has a bandwidth of 26 kHz to 4 MHz. Phase-sensitive detection (PSD) was then applied with a lock-in amplifier (Princeton Applied Research, TN, Model 5317) to record EPR absorption in the first-derivative mode. Two kinds of modulation signals were applied to the microwave signal generator to modulate the carrier frequency. A function generator (Agilent Technologies 33120A, CA) was used to give a modulation signal for EPR detection and a reference signal for the lock-in amplifier. Another signal generator (19.8 kHz) was used for ATC to adjust the resonance

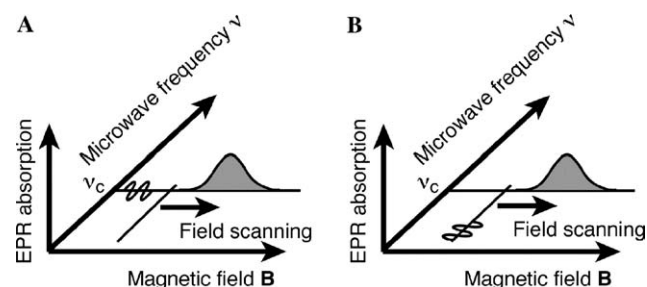


Fig. 1. Concepts of CW-EPR spectroscopy using frequency modulation (A) and conventional field modulation (B). Both methods use field scanning to record the first-derivative EPR absorption. The microwave carrier frequency ν_c in both methods is constant.

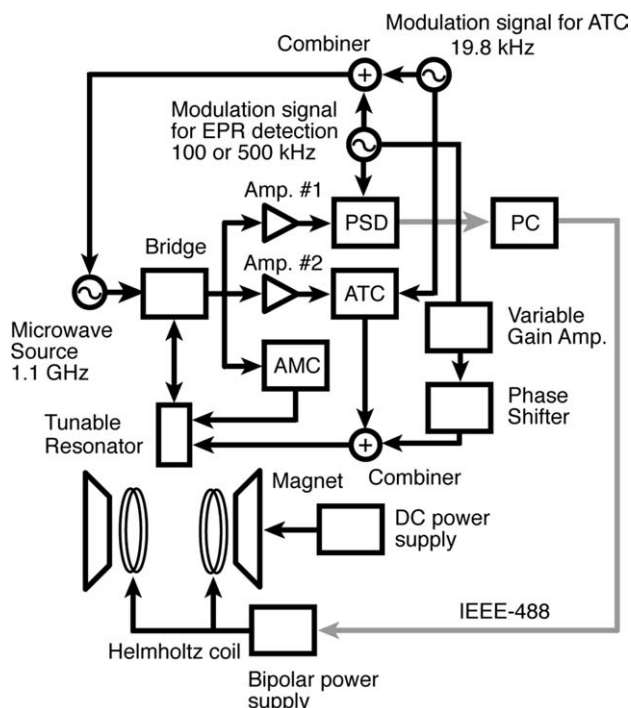


Fig. 2. Block diagram of a 1.1-GHz continuous-wave EPR spectrometer using frequency modulation. The automatic tuning control (ATC) system tunes the resonance frequency of the tunable resonator to the microwave carrier frequency. A modulation signal (100 or 500 kHz) is added to the control voltage of the ATC circuit. To adjust the deviation and phase of the instantaneous resonance frequency, the magnitude and phase of the modulation signal are carefully adjusted with a variable-gain amplifier and phase shifter.

frequency of the resonator to the microwave carrier frequency. An electronically tunable surface-coil-type resonator operating at 1.1 GHz and the ATC system were used, and the resonance frequency of the resonator was automatically adjusted to the microwave carrier frequency by the ATC system. For the applied signal at the modulation frequency (100 or 500 kHz), this signal is not controlled by negative feedback control. Thus, the amplitude and phase of the applied signal at the modulation frequency were carefully adjusted with a variable-gain amplifier and a phase shifter to minimize the microwave reflection at the resonator. The digital data for first-derivative EPR absorption were transferred from the lock-in amplifier with a LabVIEW-based control program and an IEEE-488 interface bus. This spectrometer can be used for field and frequency modulation by changing the connection of the modulation signal.

To improve the resolution of the modulation-induced sidebands in the spectra, higher modulation frequencies are desirable. While Kälin et al. [12] used 1-MHz modulation to record the first-derivative EPR spectra, we used 500-kHz modulation because of technical limitations due to the frequency modulation scheme in our spectrometer setup. Our spectrometer was less stable than a conventional spectrometer with field modulation.

In addition, 1 MHz is right at the higher edge of the frequency band of the lock-in amplifier we used. We are trying to improve the resolution of the spectra at higher modulation frequencies but have not yet overcome some technical difficulties. The 500-kHz modulation frequency, however, is higher than the frequency corresponding to the linewidth of the LiPc crystals measured (392 kHz). The resolution of the modulation-induced sidebands depends on the modulation frequency and the linewidth of each sideband. If we can overcome the technical difficulties that kept us from using higher modulation frequencies, the resolution of the sidebands will be improved.

2.4. Tunable resonator

The electronically tunable surface-coil-type resonator consists of a single-turn coil (10 mm in diameter) and a parallel transmission line formed by 50- Ω coaxial lines [25]. The tunable resonator has tuning and matching networks, and these circuits involve varactor diodes (Toshiba, Tokyo, 1SV186). By applying a reverse-bias potential to the varactors, we can remotely control the circuit parameters of the resonator, and thus the resonance frequency and impedance-matching between the resonator and the 50- Ω coaxial line connected to the microwave bridge. The resonance frequency of the tunable resonator used in our experiments can be adjusted with a coefficient of 1.26 MHz/V at a reverse-bias potential of 8 V. The resonance frequency and the unloaded quality factor of the resonator were 1125 MHz and 260, respectively. The efficiency of generating an RF magnetic field was $77 \mu\text{T}/\text{W}^{1/2}$ (the microwave magnetic field at the sample was 4.2 μT when the applied microwave power was 4.7 dBm). Additional details regarding this resonator, such as the energy distribution and dissipation, have been reported elsewhere [28].

3. Results

3.1. Measured EPR spectra

We measured the EPR spectra in both modulation schemes and compared the spectral lineshapes. The measured spectra were remarkably different at a higher modulation frequency and with a larger magnitude of modulation. Figs. 3 and 4 show the EPR spectra measured with the frequency modulation scheme at modulation frequencies of 100 and 500 kHz, respectively. The frequency deviation changed from 392 kHz to 2.352 MHz (peak-to-peak). These values correspond to the linewidth of the measured sample (14 μT) and a sixfold greater magnitude of modulation. Over-modulation makes the linewidth broader, as is usually observed when the modulation frequency is lower than the

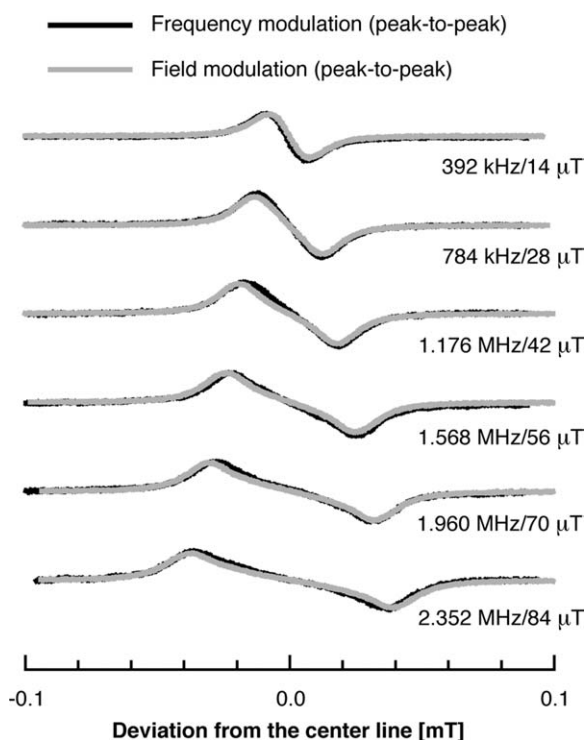


Fig. 3. EPR spectra of lithium phthalocyanine (LiPc) crystals measured at a modulation frequency of 100 kHz.

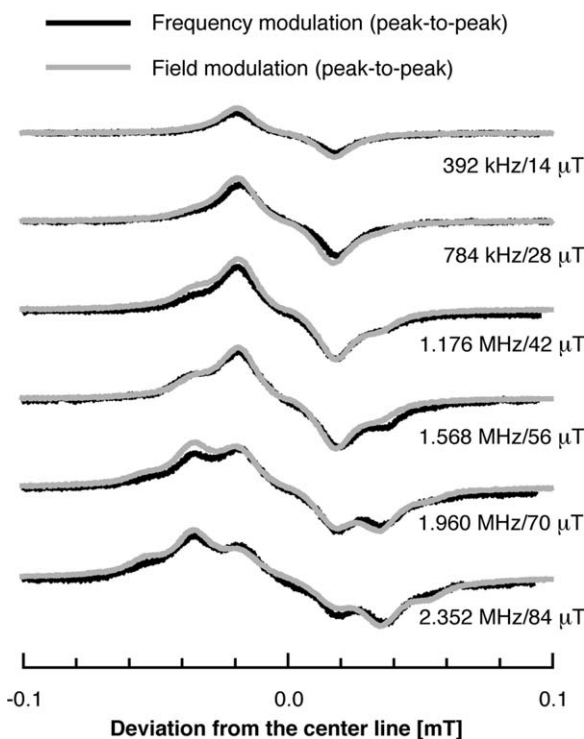


Fig. 4. EPR spectra of lithium phthalocyanine (LiPc) crystals measured at a modulation frequency of 500 kHz.

frequency that corresponds to the linewidth (Fig. 3). In contrast, the modulation-induced sidebands are resolved in over-modulation, when the modulation frequency is

higher than the frequency that corresponds to the linewidth (Fig. 4). The sidebands appear at specific magnetic fields in which the space between the discrete fields corresponds to the modulation frequency. In our experiments and simulation, this value is $18\mu\text{T}$ for a modulation frequency of 500 kHz. In Fig. 4, the sidebands at these specific fields follow the theoretical prediction. When the magnitude of modulation is similar to the linewidth, the first sideband is dominant. However, the second sideband is distinct when the frequency deviation in frequency modulation is increased, as shown in Fig. 4.

The lineshape of the frequency modulation scheme in CW-EPR spectroscopy should be compared to that of the field modulation scheme. Fig. 3 shows the EPR spectra of the same sample measured with conventional field modulation at a modulation frequency of 100 kHz. The measured spectra were quite similar to those in the frequency modulation scheme. There is no significant difference in the spectral lineshapes at a lower modulation frequency [16,17]. However, the spectra measured at a modulation frequency of 500 kHz in the field modulation scheme differ from those in the frequency modulation scheme. Since the range of detectable frequencies for the lock-in amplifier used is up to 1 MHz, and the bandwidth of the amplifier used after envelope detection in the microwave bridge is 26 kHz to 4 MHz, this bandwidth is broad enough for the modulation signal at 500 kHz. Thus, the limited bandwidths in the spectrometer setup do not create any artifact signals. The spectra measured with a small magnitude of modulation in both schemes at 100 kHz (Fig. 3) show a normal first-derivative EPR lineshape without any spectral distortion. This means that our spectrometer was appropriately set to measure the spectra. The comparison of the spectra in Fig. 4 resolves a long-standing problem in CW-EPR spectroscopy: spectral lineshapes of first-derivative EPR absorption are not equivalent in field and frequency modulation.

3.2. Numerical simulation

In the numerical simulation of the EPR spectra, we assumed negligible saturation in both the field modulation and frequency modulation schemes. We used Eq. (65) in [12] for the spectrum in the field modulation scheme. Since negligible saturation was assumed in the simulation, the lineshape depends on the modulation amplitude, the modulation frequency, and the spin–spin relaxation time T_2 in both modulation schemes. A numerical simulation of EPR spectra supports our experimental evidence. Fig. 5 shows simulated EPR spectra with various magnitude of modulation that correspond to the experiments in Fig. 4. Kälín et al. [12] reported a theory to describe the sidebands in CW-EPR spectroscopy in field and frequency modulation by introducing

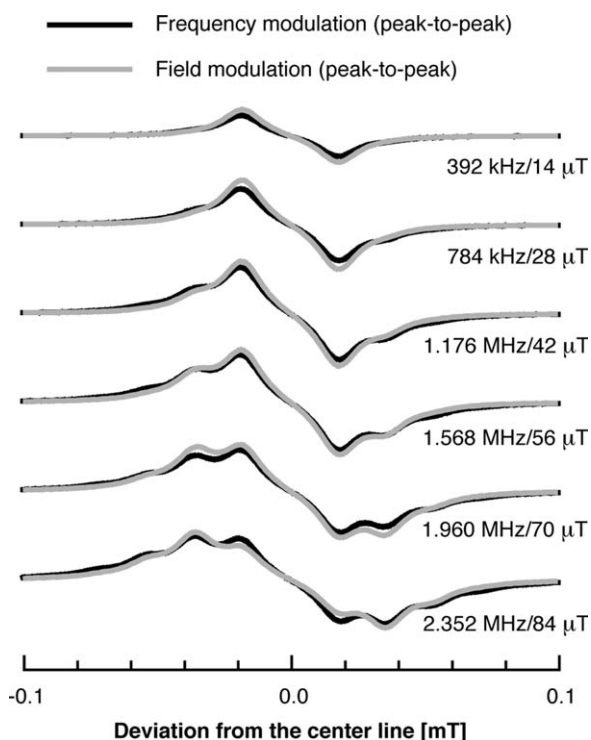


Fig. 5. Simulated EPR spectra for a modulation frequency of 500 kHz. In the numerical simulation, the spin–spin relaxation time T_2 and the full linewidth between the half-amplitude points of the Lorentzian lineshape were assumed to be $0.3 \mu\text{s}$ and $18 \mu\text{T}$, respectively. The signal intensity of each spectrum was adjusted to the measured one (Fig. 4). The sidebands were calculated according to [12]. We assumed negligible saturation in both the field modulation and frequency modulation schemes.

multiple photon transition. The first-derivative absorption spectra in Fig. 5 were calculated based on [12]. These spectra were numerically obtained by convolution of the Lorentzian lineshape and modulation-induced sidebands, which are a series of a δ -function. While an EPR spectrum consists of several sidebands, these are not resolved at a lower modulation frequency, as shown in Fig. 3. However, these sidebands are resolved when the modulation frequency is increased, as shown in Fig. 4 [12]. The calculated lineshapes in Fig. 5 reasonably agreed with the measured ones in Fig. 4, when appropriate parameters such as spin–spin relaxation time T_2 and the full linewidth between the half-amplitude points of the Lorentzian lineshape were assumed. The simulated EPR spectra agree well with the measured ones.

4. Discussion

We used field-swept spectroscopy with frequency modulation detection, and thus achieved a somewhat skewed frequency modulation scheme. The sample used in the present study was LiPc, which has a narrow EPR linewidth, i.e., long relaxation time (T_2). We thereby

hoped to achieve intensified effects, but in the future we will use samples with a shorter relaxation time, such as transition ions. In the present study, we used low magnetic field detection, i.e., L-band EPR spectroscopy. The frequency modulation scheme potentially has no limitations regarding the microwave frequency or the magnetic field. However, the development of an electronically tunable microwave resonator should be a key technical issue at higher frequencies. Another technical limitation is the magnitude of the frequency deviation in the microwave source. In fact, the maximum frequency deviation is always limited at a certain value that depends on the microwave carrier frequency. While Kälin et al. [12] reported the saturation characteristics of modulation-induced sidebands in the field modulation scheme, we did not investigate this aspect of the frequency modulation scheme. This should be considered in future investigations regarding the frequency modulation scheme.

CW-EPR spectroscopy using frequency modulation can provide a different physical perspective in electron-spin-related phenomena, i.e., behavior in the frequency domain for unpaired electron spins. This should promote the application of the frequency modulation method in CW-EPR spectroscopy to spin physics and related studies. According to the equation of magnetic resonance, $g\mu_B B = h\nu$, the magnetic field B is linearly proportional to microwave frequency ν (μ_B is the Bohr magneton and h is Planck's constant). This is only valid for the single quantum transition scheme. In fact, Kälin et al. [12] reported that modulation-induced sidebands in the spectrum are multiple photon transitions when the modulation frequency exceeds the linewidth. Our experimental results suggest that differences between field-modulation spectra and frequency-modulation spectra would be observed when the magnitude of modulation is more than four or five times the linewidth of the measured sample and the modulation frequency is higher than the frequency corresponding to the linewidth.

It has been reported that field-swept and frequency-swept spectra reflect different magnetic susceptibilities [11]. While it is clear on a theoretical basis that the susceptibilities measured by the field-swept and frequency-swept methods are different in principle, it is not so clear that they are experimentally distinguishable on a practical level. Since we performed a field sweep on top of frequency modulation, it is important to figure out which thermodynamic susceptibility we are actually measuring. Because of the small modulation, there is no significant difference between spectral lineshapes in the measured and calculated spectra. The magnitude of modulation was less than 0.2% of the center field in the field modulation scheme and of the microwave carrier frequency in the frequency modulation scheme. This could be a reason that the difference between field-dependent and frequency-dependent susceptibilities was

not detectable in our experiments. While the effect of susceptibility was not included in our calculations, it does not give a significant error in comparison between the measured and calculated spectra. Whether the difference between field-dependent and frequency-dependent susceptibilities can actually be detected is something that requires further investigation.

Several theoretical schemes have been reported to describe EPR spectra as detected by frequency modulation. First, the quantum mechanical perturbation approach is an effective way to calculate the resonance field. Second, it is possible to directly compute the magnetic fields at which resonance occurs at a fixed microwave frequency using the eigenfields method developed by Belford et al. [29]. Third, a recent theoretical paper has shown that semi-classical treatment successfully predicts side-band behavior in a frequency modulation scheme [12]. We could evaluate EPR spectra with frequency modulation by following Eq. (75) in [12] and convoluting the component spin packets. The calculated EPR displays were in good agreement with frequency modulated spectra. Although the approach in [12] did not take into account the thermodynamic susceptibility that is detectable by two different modulation schemes, the good agreement between the theoretical and experimental spectra in the present study should be valid within certain experimental limits.

Finally, the experimental findings in this report suggest that field and frequency modulation do not give equivalent results in CW-EPR spectroscopy. Our experimental results may be useful in future studies of electron-spin-related phenomena.

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