Journal of Magnetic Resonance 287 (2018) 123–127

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

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

Enhanced accuracy of the microwave field strength measurement in a CW-EPR by pulsed modulation technique

B. Rakvin *, D. Carić, M. Kveder

Ruđer Bošković Institute, Division of Physical Chemistry, Bijenička 54, Zagreb, Croatia

ARTICLE INFO

Article history:
Received 11 December 2017
Revised 9 January 2018
Accepted 10 January 2018
Available online 11 January 2018

Keywords:
EPR spectroscopy
Microwave field strength
Modulation spectrum
Amplitude modulation EPR
Bloch-Siegert shift

ABSTRACT

The microwave magnetic field strength, B_1, in the cavity of a conventional continuous wave electron paramagnetic resonance, CW-EPR, spectrometer was measured by employing modulation sidebands, MS, in the EPR spectrum. MS spectrum in CW-EPR is produced by applying the modulation frequency, ω_{rf}, which exceeds the linewidth, δB, given in frequency units. An amplitude-modulated CW-EPR, AM-CW-EPR, was selected as detection method. Theoretical description of AM-CW-EPR spectrum was modified by adding Bloch-Siegert-like shift obtained by taking into account the cumulative effect of the non-resonant interactions between the driving fields and the spin system. This approach enables to enhance the precision of B_1 measurement. In order to increase the sensitivity of the method when saturation effects, due to higher intensity of B_1, decrease the resolution of AM-CW-EPR spectrum, detection at the second harmonic of CW-EPR has been employed.

1. Introduction

The microwave magnetic field strength, B_1, as well as closely related Rabi frequency ($\omega_1 = \gamma_e B_1$) of a spin system in the microwave field, MW, are essential parameters for all quantitative measurements in EPR spectroscopy. In recent years studies of spin system containing very long relaxation times (transverse, T_2 and longitudinal, T_1) are of interest due to their potential application in quantum information technologies. One of the most often addressed model cases in these studies is the resonant interaction between the bichromatic field (transverse MW field and longitudinal radiofrequency (RF) field) and two level spin system (spin qubit) experiencing the Zeeman magnetic field. Early theoretical study of modulation effect in EPR spectroscopy was based on semi-classical approach by applying modified Bloch equations [1]. However, recently the description was revised and modulation effects in the continuous wave EPR, CW-EPR, spectroscopy explained by introducing multi-photon transitions [2,3]. By using quantized radiation fields it was shown [2,3] that modulation sidebands, MS, appearing in the EPR spectrum when the modulation frequency, ω_{rf}, used in CW-EPR exceeds the linewidth, δB, can be described by the multi-photon transitions. In these transitions one MW σ^+ photon is absorbed from the MW radiation field and an arbitrary number k of RF π photons are absorbed from or emitted to the modulation RF field ($\sigma^+ + k \times \pi$).

In the present consideration among the various different methods [4–11] for estimation of B_1, the experimental method with pulsed modulation detection proposed several decades ago [12] will be discussed and revised within recently suggested multiple photon description of CW-EPR spectra. The method is based on the measurements of splitting between the first sideband signals [10,11], d_1, under the small modulation index $z = 2\omega_2/\omega_{rf}$ ($2\omega_2$ corresponds to the amplitude of RF field), ($z \ll 1$) [12]

$$\left(\frac{d_1}{2}\right)^2 = \frac{\omega_{rf}^2}{\gamma_e^2} - B_1^2 \tag{1}$$

One can measure d_1 for several values of ω_{rf}, and from the intercept on the abscissa of the plot $(d_1/2)^2$ versus ω_{rf}^2 the value of B_1 can be obtained in accord with Eq. (1).

This approach shows several advantages in comparison with other methods [4,5,8,9]. As was shown earlier the method [12] requires no additional calibration procedure and yields B_1 values directly in a wide range of microwave power. Moreover, the pulsed modulation technique can be performed by employing standard audiofrequency lock-in amplifier for detection of the dc signal component rather than the first harmonic component of a sideband spectrum. It could be noted that detection of the dc signal of sidebands spectrum is possible with low frequency pulse modulation (within range of 0–100 kHz as expected for lock-in amplifier included in a standard CW-EPR spectrometer) in

* Corresponding author.
E-mail address: rakvin@irb.hr (B. Rakvin).

https://doi.org/10.1016/j.jmr.2018.01.006
1090-7807/

comparison with the first harmonic detection [10,11] where significantly large ω_{rf} is usually required ($\omega_{rf} \sim 1$ MHz) for producing sideband's splitting and lock-in detection at the same frequency [2]. However, there is some limitation in this method due to approximation in theoretical description, which is based on the semi-classical rotation frame model [2]. The sideband's splitting taken for close sideband's resonance (where condition ($\omega_1/\omega_{rf} \ll 1$) is not preserved and transforms towards the condition ($\omega_1/\omega_{rf} < 1$)) deviate from the straight line in the plot d_1^2 versus ω_{rf}^2 [12]. Therefore, these experimental points were avoided in the process of evaluation of the B_1.

2. Effect of Bloch-Siegert-like shift on MS spectrum

2.1. Amplitude-modulated CW-EPR with Bloch-Siegert-like shift

The experimental method of pulsed modulation detection employed earlier generally coincides with more recently suggested method of amplitude-modulated CW-EPR, AM-CW-EPR [13,14]. Thus, in order to simulate experimental modulation spectra detected previously [12] and to evaluate more accurately the corresponding B_1, the theoretical description of the AM-CW-EPR spectrum for an individual homogeneous line is required. Presently suggested theoretical description [13,14] includes B_1 exclusively in the saturation term, while the splitting between sidebands is lacking the B_1 dependence and it is proportional only to the multiple of modulation frequency ($k\omega_{rf}$). Therefore, here presented study improves this description by introducing Bloch-Siegert-like shift, Δ_k, of the energy levels obtained from the expanded Hamiltonian for resonant multiple photon transitions [2,3,15,16]. Following recent theoretical description of spin dynamics which can be treated with frequency parameters in the range of CW-EPR spectroscopy [16], it is convenient to introduce two different regimes of the spin dynamics such as: "weak modulation near the Rabi resonance" and "strong and fast modulation" with the corresponding values of the applied RF modulation ($\omega_2 \ll \omega_1 \approx \omega_{rf}$) and ($\omega_2 > \omega_1 \ll \omega_{rf}$), respectively. For each of these regimes the corresponding Δ_k was suggested and calculated. In accord with the selection of RF for the "strong and fast modulation" regime Δ_k was calculated [15,16] up to the second order contribution in small parameter ω_1/ω_{rf}. By employing these results and an additional term of Δ_k for the evaluation a homogenous EPR line [16] the new description of AM-CW-EPR spectrum [13,14] is here suggested

$$P = \sum_{k=-\infty}^{\infty}\left[\frac{\omega_1 T_2 J_k^2(z)}{1+\omega_1^2 T_1 T_2 J_k^2(z) + (\Omega_s - k\omega_{rf} + \Delta_k)^2 T_2^2} - \frac{\omega_1 T_2 J_k^2(0)}{1+\omega_1^2 T_1 T_2 J_k^2(0) + (\Omega_s - k\omega_{rf} + \Delta_k)^2 T_2^2}\right] \quad (2)$$

$$\Delta_k = \frac{\omega_1^2}{4\omega_{mw}} + \left(\frac{\omega_1^2}{2\omega_{rf}}\right)\sum_{l\neq k}\frac{J_l^2(z)}{(k-l)}$$

where $z = 2\omega_2/\omega_{rf}$, $J_k(z)$ is the Bessel function of the first kind and order k, $\Omega_s = \omega_s - \omega_{mw}$ and $\omega_s = \gamma_e B_0$. For weak MW fields, as commonly used in CW-EPR the first term in Δ_k is small and can be neglected. It can be shown that $\Delta_{-k} = -\Delta_k$ and there is no shift for $\Delta_0 = 0$ (k = 0, centerband) while the largest contribution to the splitting is expected between the first sidebands in comparison with the splitting between the second and higher order of sidebands. From the Eq. (2) one can easily evaluate the new corrected splitting between sidebands peaks as:

$$\left(\frac{\gamma_e d_k}{2}\right) = k\omega_{rf} - \Delta_k \quad (3)$$

In order to compare Eqs. (1) and (3), Eq. (3) can be transformed in the form of Eq. (1)

$$\left(\frac{d_1}{2}\right)^2 = \frac{\omega_{rf}^2}{\gamma_e^2} - B_1^2\sum_{l\neq 1}\frac{J_l^2(z)}{(1-l)} + \frac{1}{\gamma_e^2}\left(\frac{\omega_1}{2\omega_{rf}}\right)^2\left(\sum_{l\neq 1}\frac{J_l^2(z)}{(1-l)}\right)^2 \quad (4)$$

The obtained result approaches the result derived from the rotation frame model given in Eq. (1) when assuming conditions for strong and fast modulation ($z \ll 1$, and $\omega_1/\omega_{rf} \ll 1$). Under these conditions and by taking the leading terms in the Bessel sum approaching unit value the Eq. (4) is further simplified

$$\left(\frac{d_1}{2}\right)^2\left(1-\frac{z^2}{4}\right)^{-2} \approx \frac{\omega_{rf}^2}{\gamma_e^2}\left(1+\frac{\Delta_1^2}{\omega_{rf}^2}\right)\left(1-\frac{z^2}{4}\right)^{-2} - B_1^2 \quad (5)$$

The obtained relation increases accuracy of a description of the intercept on the abscissa of the plot $(d_1/2)^2$ versus ω_{rf}^2 in comparison with the earlier description given by Eq. (1). The effect of these corrections can be easily followed by presenting the data using scaled plot $(d_1/2)^2(1-z^2/4)^{-2}$ versus $(\omega_{rf}/\gamma_e)^2(1-z^2/4)^{-2}$ $(1+\Delta_1^2/\omega_{rf}^2)$. This approach includes the change of z and Δ_1 parameters as is expected for measurements at different ω_{rf} values. Additionally, the similar analyses can be provided for the second spin dynamics regime "weak modulation near the Rabi resonance" and the corrected separation between the sidebands peaks is expected as follows [16]

$$\left(\frac{d_1}{2}\right)^2 = \frac{\omega_{rf}^2}{\gamma_e^2}\left(1-\frac{\Delta(1)}{\omega_{rf}}\right)^2 - B_1^2$$

$$\Delta(1) = \frac{\omega_2^2\sin^2\theta}{2\omega_{rf}}\left[\sum_{n\neq 0}\frac{1}{n}(J_n^2(a) + J_n(a)J_{n-2}(a)) + \sum_{n\neq -2}\frac{1}{n+2}(J_n^2(a) + J_n(a)J_{n+2}(a))\right] \quad (6)$$

where $a = (2\omega_2/\omega_{rf})\cos\theta$, $\sin\theta = \omega_1/(\omega_1^2 + \Omega_s^2)^{1/2}$ and $\cos\theta = \Omega_s/(\omega_1^2 + \Omega_s^2)^{1/2}$. In this dynamics regime $\Delta(1)$ is calculated up to the second order contribution by assuming $(\omega_2/\omega_{rf})\sin\theta \ll 1$ as a small parameter. The advantage of this theoretical result is that one can describe the splitting between sidebands when RF modulation is in the vicinity of Rabi resonance ($\omega_1 \approx \omega_{rf}$) [16,17]. It is expected that d_1 exhibits minimum at resonance condition ($\omega_1 = \omega_{rf}$) and amplitudes of low-field and high-field sideband are not equal as was demonstrated in the time resolved EPR experiment [17].

Thus, the choice of the appropriate relation to express measured data in terms of d_1^2 versus ω_{rf}^2 at constant microwave power depends on the characteristic relaxation parameters T_1 and T_2 of spin system and on the applied regime of spin dynamics (ω_2, ω_{rf} and ω_1). One expects that for more reliable measurements of d_1 it is convenient to use larger values of, $d_1 \sim 2\omega_{rf}$ than the smaller values of d_1 near the low limit, $d_1 \approx \delta B$. This requires measurements in the fast motional regime, which will be in the focus of the further consideration. In the fast modulation regime one obtains good approximation by employing the plot $(d_1/2)^2$ versus $(\omega_{rf}^2/\gamma_e^2)$. In order to increase the accuracy of B_1 the contribution of Bessel functions for known parameters ω_2 and ω_{rf} of applied modulation frequency should be calculated (Eq. (5)). Moreover, one can also simulate complete experimental AM-CW-EPR spectrum by employing Eq. (2) to evaluate B_1 in which case two additional parameters (T_1 and T_2) are required.

2.2. Simulation of AM-CW-EPR with Bloch-Siegert-like shift

The expression given in Eq. (2) can be used to simulate AM-CW-EPR spectra of a homogeneous line at various modulation frequencies and also to examine dependence of these spectra on the