1 January 1999

ELSEVIER

Chemical Physics Letters 299 (1999) 69–74

CHEMICAL PHYSICS LETTERS

A novel two microwave field ESR implemented by double field modulation

Miroslav Peric *, Christopher D. McMullen, Victor Andrade, Barney L. Bales

Department of Physics and Astronomy and The Center for Cancer and Developmental Biology, California State University at Northridge, Northridge, CA 91330-8268, USA

Received 1 June 1998; in final form 26 October 1998

Abstract

A theoretical and experimental study of the application of two microwave fields to the case of an inhomogeneously broadened electron spin resonance (ESR) line with neglect of spin diffusion is presented. The two microwave field ESR (TMFESR) may be implemented as a simple version of the double-modulation ESR method provided the modulation index is small. When applied to an inhomogeneously broadened ESR line, the technique yields a response whose width is twice the width of the spin packet. The E' defect in γ-irradiated vitreous silica was studied by TMFESR yielding a value of $T_2 = 23.6$ μs, in agreement with time-domain ESR measurements. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

It is well known that homogeneous broadening of the electron spin resonance (ESR) spin packet reflects the dynamics of the spin system; however, the homogeneous line is often obscured by inhomogeneous broadening [1]. Detailed information on homogeneous linewidth can be extracted by pulsed ESR techniques [2], but pulsed instruments are not widely available due to their cost and sophistication. For the majority of the laboratories employing continuous wave spectrometers, a simple technique to extract the homogeneous component of an inhomogeneously broadened line would be useful. It has been known for some time that a continuous wave technique, the double modulation of electron spin resonance (DMESR), may also be used to extract narrow homogeneous spin packet lines from an inhomogeneously broadened ESR line [3]. The method is based on applying two magnetic field modulations one at a fixed (observing) frequency and the other with a swept (pumping) frequency. DMESR has been applied to a variety of problems [4–10]. ESR triple modulation methods [9] have also been introduced, allowing measurements of extremely short values of T_2 [11,12].

The effects of field modulation are naturally discussed in terms of the modulation index

$$\beta = \gamma B_m / \omega_m ,$$

where B_m is the amplitude of the modulation at frequency ω_m, and γ is the gyromagnetic ratio of the electron. Most of the previous work [4–8,10] involved magnetic-field modulation indices larger than five that are large enough to introduce complicated,

* Corresponding author. E-mail: miroslav.peric@csun.edu

0009-2614/99/$ - see front matter
PII: S0009-2614(98)01242-1

sometimes misinterpreted results. Here we present a new double modulation method, called the two microwave field ESR (TMFESR), which is based on the use of low modulation indices, $\beta < 0.1$. TMFESR can be used to extract the spin packet linewidth from an inhomogeneously broadened ESR line. In this Letter, we show that proper implementation of the TMFESR techniques yields unambiguous results.

2. Experimental

A sample of vitreous silica, irradiated to 24.4 Mrad with ^{60}Co gamma radiation was purchased from Wilmad Glass (Buena, New Jersey). All measurements were carried out at room temperature, $T = 22°C$. ESR and TMFESR spectra were measured on a Bruker ESP 300E spectrometer additionally equipped. The pumping field was provided by a Wavetek 50-MHz pulse/function generator Model 166, while the observing frequency was generated by an EGG Parc Model 124 Lock-in amplifier. The two frequencies were mixed and then amplified by an Amplifier Research Model 50A220 radio frequency amplifier, which drove a small flat coil internal to the cavity (standard Bruker ER 4102 ST cavity). Signal acquisition was done with an IBM 486 computer equipped with Real Time Devices ADA2000 interface board.

3. Theory

We employ the formalism of the Bloch equations in complex form [13], in which the real xy plane of the coordinate system fixed in the laboratory frame is replaced by a complex plane so that the magnetization has components $(U + \mathrm{i}V, W)$, where U and V are the real (dispersion) and imaginary (absorption) parts of the transverse magnetization, respectively and W is the longitudinal magnetization. A single rotating microwave field B_1 in the xy plane and static magnetic field B_0 along the z axis are combined into a total field with components $(B_1 \exp(-\mathrm{i}\omega t), B_0)$, where ω is the microwave field frequency. After adding the phenomenological relaxation terms and transforming into a rotating frame we get:

$$\frac{\mathrm{d}}{\mathrm{d}t}(U + \mathrm{i}V) = -\mathrm{i}(U + \mathrm{i}V)\gamma B_0 + \mathrm{i}W\gamma B_1 \exp(-\mathrm{i}\omega t) - \frac{(U + \mathrm{i}V)}{T_2}, \tag{1a}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}W = \frac{1}{2\mathrm{i}}\left[(U - \mathrm{i}V)\gamma B_1 \exp(-\mathrm{i}\omega t) - (U + \mathrm{i}V)\gamma B_1 \exp(\mathrm{i}\omega t)\right] - \frac{W - W_{\mathrm{eq}}}{T_1}, \tag{1b}$$

where W_{eq} is the thermal equilibrium value of W, T_1 is the spin–lattice relaxation time, and T_2 is the spin–spin relaxation time. In Eqs. (1a) and (1b), the modulation is included by replacing the static magnetic field, B_0, by the proper term for the modulated magnetic field [13].

Magnetic-field modulation is equivalent to frequency modulation of the microwave field [14]. The frequency modulated field is represented by a superposition of monochromatic sideband fields separated from each other by the modulation frequency. The amplitudes and phases of the sidebands are given by the Bessel functions of the modulation index β. Small values of β for both observing and pumping field modulations will produce a sideband pattern that consists of the centerband and very weak first sidebands, the other sidebands being negligible [15]. Thus, the experiment is performed with only two monochromatic microwave fields acting upon an inhomogeneous ESR line, which is the simplest case of double modulation, both theoretically and experimentally. Replacing $B_1 \exp(-\mathrm{i}\omega t)$ with a sum of two microwave fields $B_\mathrm{o} \exp(-\mathrm{i}\omega_\mathrm{o} t) + B_\mathrm{p} \exp(-\mathrm{i}\omega_\mathrm{p} t)$ in Eqs. (1a) and (1b) we have Bloch equations that describe the TMFESR, where B_o and B_p are the amplitudes of the observing and pumping fields of frequency ω_o and ω_p, respectively. Having assumed weak microwave fields, the response of the spin system will be given as a power expansion of the field strengths $B_o^n B_p^m$, which we truncate at third order as follows:

$$U + \mathrm{i}V = (u + \mathrm{i}v)_o \exp(-\mathrm{i}\omega_o t) + (u + \mathrm{i}v)_p \exp(-\mathrm{i}\omega_p t) + (u + \mathrm{i}v)_{2o\text{-}p} \exp[-\mathrm{i}(2\omega_o - \omega_p)t] + (u + \mathrm{i}v)_{2p\text{-}o} \exp[-\mathrm{i}(2\omega_p - \omega_o)t], \quad (2a)$$

$$W = w_0 + w_{o\text{-}p} \exp[-\mathrm{i}(\omega_o - \omega_p)t] + w_{p\text{-}o} \exp[-\mathrm{i}(\omega_p - \omega_o)t], \quad (2b)$$

where w_0 is the zeroth order of W in the rotating frame. The resulting set of coupled differential equations becomes:

$$\frac{\mathrm{d}}{\mathrm{d}t}(u + \mathrm{i}v)_o = -\mathrm{i}(\omega_0 - \omega_o)(u + \mathrm{i}v)_o + \mathrm{i}(w_0 \gamma B_o + w_{o\text{-}p} \gamma B_p) - \frac{(u + \mathrm{i}v)_o}{T_2}, \quad (3a)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(u + \mathrm{i}v)_{2o\text{-}p} = -\mathrm{i}[\omega_0 - (2\omega_o - \omega_p)] \times (u + \mathrm{i}v)_{2o\text{-}p} + \mathrm{i}w_{o\text{-}p} \gamma B_o - \frac{(u + \mathrm{i}v)_{2o\text{-}p}}{T_2}, \quad (3b)$$

$$\frac{\mathrm{d}}{\mathrm{d}t} w_0 = \frac{1}{2\mathrm{i}} [(u - \mathrm{i}v)_o \gamma B_o + (u - \mathrm{i}v)_p \gamma B_p - (u + \mathrm{i}v)_o \gamma B_o - (u + \mathrm{i}v)_p \gamma B_p] - \frac{w_0 - W_{eq}}{T_1}, \quad (3c)$$

$$\frac{\mathrm{d}}{\mathrm{d}t} w_{o\text{-}p} = \frac{1}{2\mathrm{i}} [(u - \mathrm{i}v)_p \gamma B_o + (u - \mathrm{i}v)_{2p\text{-}o} \gamma B_p - (u + \mathrm{i}v)_{2o\text{-}p} \gamma B_o - (u + \mathrm{i}v)_o \gamma B_p] - [1 - \mathrm{i}T_1(\omega_o - \omega_p)] \frac{w_{o\text{-}p}}{T_1}, \quad (3d)$$

and the equations obtained from Eqs. (3a), (3b) and (3d) by interchanging o and p, where $\omega_0 = \gamma B_0$. We observe the steady-state solution of these equations, i.e., the time derivatives are set equal to zero. In TMFESR measurements of an inhomogeneous ESR line with narrow spin packets the signal must be parametrized with the local field ω_L and the integral performed over the inhomogeneous distribution function $g(\omega_L)$.

4. Results and discussion

4.1. Computer simulations

Eqs. (3) with the time derivatives equal to zero were solved numerically for an inhomogeneous ESR line. Spin diffusion was neglected, and the difference in resonance fields of two successive spin packets was always less than the full linewidth at half height (FLWHH) of the spin packet, whose lineshape is Lorentzian. The inhomogeneous distribution function $g(\omega_L)$ was assumed to be a Gaussian lineshape and the system of linear equations was solved by the LU Decomposition method [16].

If we were to select a pumping frequency and sweep the observing frequency, as is common in optics [17], we would observe a hole burned into the response at the position of the pumping frequency. In ESR, since a lock-in amplifier is usually employed, it is more convenient to fix the observing frequency and sweep the pumping frequency. In this case, one observes a constant ESR signal until the pumping frequency comes into the vicinity of the observing frequency. Such a TMFESR response is shown in Fig. 1. The response in Fig. 1 was simulated using 0.01 and 0.02 mG for the amplitudes of the observing and pumping fields, respectively. The observing frequency was 210 kHz while the pumping frequency was swept from 20–400 kHz. The relaxation times were chosen to be $T_1 = 150$ μs and $T_2 = 25$ μs which correspond to literature values for the E′ center in irradiated silica [18], while the inhomogeneous ESR linewidth was very broad, $T_2^* = 10$ ns.

Interestingly, after fitting the TMFESR signal to a Lorentzian lineshape one finds that the linewidth of the TMFESR 'hole' is exactly a factor of 2 larger

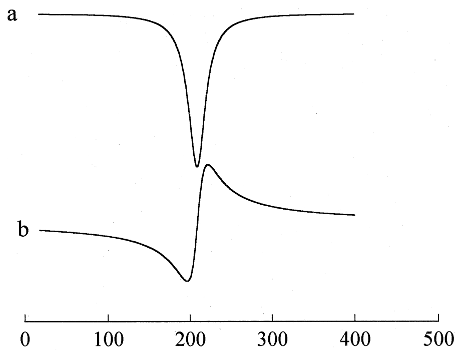

Fig. 1. Simulation of the hole burning phenomenon in an inhomogeneously broadened ESR line observed by a weak fixed observing microwave field $B_o = 0.01$ mG at 210 kHz in the presence of a weak pumping microwave field $B_p = 0.02$ mG swept from 20 to 400 kHz. The linewidth of the ESR line is 31.8 MHz ($T_2^* = 10$ ns), the electron relaxation times of the spin packet are $T_2 = 25$ μs and $T_1 = 150$ μs. The density of spin packets is 643 MHz^{-1}. (a) In-phase TMFESR spectrum. (b) Out-of-phase TMFESR spectrum.

than the spin packet width. Thus, the relaxation time T_2 is found from the relation:

$$T_2 = \frac{2}{\pi \Delta_{1/2}}, \quad (4)$$

where $\Delta_{1/2}$ is the FLWHH of the TMFESR response measured in Hz. A similar result is known in saturation spectroscopy in optics [19]. Note that the textbook expression for a Lorentzian spin packet is of the form of Eq. (4) with a factor of unity in the numerator when the FLWHH is in Hz. If the inhomogeneous line is imagined as a series of homogeneous spin packets, Lorentzian lines, of a certain linewidth, then the TMFESR is a hole burning experiment producing a 'hole' twice as broad as the spin packets. This result is the consequence of the fact that the observed signal is the convolution of two Lorentzian lines of equal linewidths, which doubles the linewidth [19]. When the phase of the reference frequency of the lock-in amplifier is set at 90° with respect to the observing modulation frequency, it has been known that a dispersion-like signal may be observed [3,20]. By considering the signal as a convolution of a modulation response function and ESR signal one may show [21] that the signal is the dispersion of the spin packet. The out-of-phase TMFESR (dispersion) signal is shown in Fig. 1b.

We emphasize that this simple result allowing the direct measurement of T_2 is only valid at small values of the modulation indices, < 0.1. At higher indices, the linewidth of the TMFESR line depends on the intensity of both microwave fields [21].

4.2. Measurements

Fig. 2 shows the ESR spectrum of the irradiated silica sample housed in the same ESR cavity with a single crystal of fluoranthenyl radical cation salt $(FA_2)^+PF_6^-$ with the reference of the lock-in amplifier in phase with the modulation. This organic conductor gives a single narrow ESR line [22,23] with a peak-to-peak linewidth of 12.2 mG. The $(FA_2)^+PF_6^-$ sample was used to insure that the index of modulation for each modulation frequency is very small, < 0.1, and that the reference phase of the lock-in amplifier was properly set. The narrow line of $(FA_2)^+PF_6^-$ permits direct observation of the two microwave sidebands. Under these conditions only the two first microwave sidebands are detected, i.e., there are only Bessel functions of order ± 1 in the modulation response function [21], Fig. 2. Note that contrary to some textbook accounts, only the two sidebands are observed; there is no central component to the resonance. The frequency of the observing modulation was chosen to be 210 kHz to

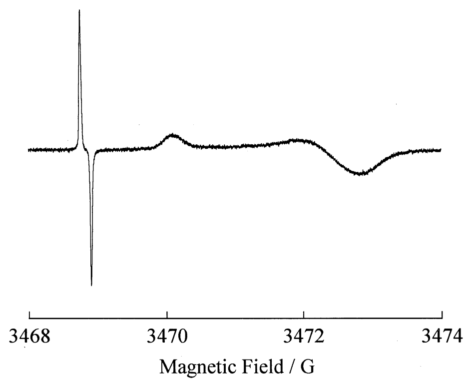

Fig. 2. In-phase ESR spectrum of irradiated vitreous silica, broad resonances near 3470 and 3472 G, and a single crystal of flouranthenyl radical cation salt $(FA_2)^+PF_6^-$, narrow resonance near 3469 G. The modulation frequency is 210 kHz. The narrow lines display the two microwave sidebands and an absence of a central component.

provide ample baseline. The in-phase TMFESR (absorption) signal is observed when the frequency of the pumping modulation is swept over the observing modulation frequency, at a fixed magnetic field position of 3472.9 G, Fig. 3. The term in-phase is with respect to the phase of the observing modulation. To determine the FLWHH of the signal, least-squares fitting was employed. The fit to the sum of the absorption of two Lorentzians was significantly better than that for a single absorption Lorentzian line. The FLWHH of the narrow Lorentzian was 27 kHz, which according to Eq. (4) corresponds to a spin–spin relaxation time of 23.6 μs which is very close to the value $T_2 = 25$ μs measured by the Eatons and coworkers [18,24]. The fit of the broader line depends on the noise, giving a FLWHH, which is about four times that of the narrow line with a relative uncertainty of 15%. This result agrees with the finding of Ref. [18] where the saturation recovery data at X- and S-bands were fit to two exponentials. Fig. 4 shows the out-of-phase TMFESR (dispersion) signal obtained by shifting the reference phase of the lock-in amplifier by 90°. The out-of-phase TMFESR signal was fit to two Lorentzian dispersion lines, yielding linewidths identical to those of the absorption signal. The wiggles on the top of the signal are caused by the beat frequency $\omega_B = \omega_o - \omega_p$.

Using the triple modulation ESR technique Miyagawa's group has studied an X-ray irradiated fused quartz [9] and an activated carbon [12]. In the triple modulation ESR technique the third modulation was used as the detecting modulation, which allows one to detect a broad spin packet using an ordinary lock-in amplifier with a working range below 100 kHz. The modulation indexes in those studies (see fig. 1d in Ref. [9]) were very small as in this work, thus the relaxation time T_2 in those experiments can be calculated using Eq. (4), or in other words they can be regarded as TMFESR experiments. The linewidth of the triple modulation ESR signal of the X-ray irradiated sample [9] was the same order of magnitude as T_2 measured in our study. The previously unexplained nature of the observed splitting of 200 kHz in the triple ESR spectra [9] can be explained by the type of detection used, that is the second-harmonic signal at the detecting frequency. If the phase-sensitive detector is driven at twice the detecting frequency and the index of modulation is small then the second-harmonic signal has only two sidebands separated by four times the detecting frequency [21].

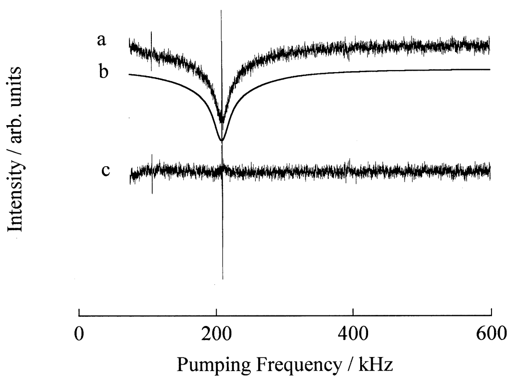

Fig. 3. (a) A typical in-phase TMFESR spectrum of γ-irradiated vitreous silica, with the field set at 3472.9 G. The observing frequency is 210 kHz and pumping frequency is swept from 61 to 586 kHz. (b) The best fit to the observed signal which is composed of the absorption of two Lorentzian lines. (c) The difference between the experimental spectrum and the best fit.

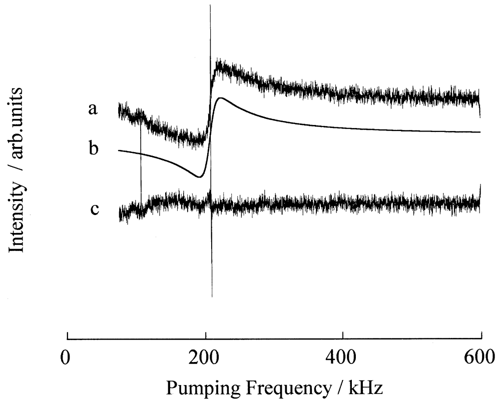

Fig. 4. (a) A typical out-of-phase TMFESR spectrum of γ-irradiated vitreous silica, with the field set at 3472.9 G. The observing frequency is 210 kHz and pumping frequency is swept from 61 to 586 kHz. (b) The best fit to the observed signal, which is composed of the dispersion of two Lorentzian lines. (c) The difference between the experimental spectrum and the best fit.

The linewidth of the TMFESR signal was measured as a function of microwave power. It was found that the narrow line broadens with increasing microwave power, while its height increases, reaches a maximum and then disappears. This disappearance is presumably caused by spin diffusion [18] and saturation.

5. Conclusions

We have shown both theoretically and experimentally that the method of two microwave field ESR (TMFESR) can be used to measure the spin–spin relaxation time T_2 in an inhomogeneously broadened ESR. An expression, Eq. (4), to calculate T_2 from the linewidth of the TMFESR signal is given. This expression is a factor of 2 larger than expected for the spin packet [25]. Experimentally, we used the double modulation ESR technique with extremely small modulation indexes for both modulations, < 0.1. The electron spin–spin relaxation time T_2 of the E′ defect in γ-irradiated vitreous silica, which was proposed as a standard for time-domain ESR [24], was measured by TMFESR and was found to be the same as that measured by time-domain ESR [18]. To measure a broad spin packet the same experiment can be performed using the technique of triple modulation ESR [9].

Acknowledgements

This research was supported by a grant from the NIH 3 R15 GM/RR494737-01S1 (to MP), SO6 GM/HD48680-03 (to BLB) and a grant from the CSUN Research and Grants Committee (to MP).

References

[1] B.L. Bales, in: L.J. Berliner, J. Reuben (Eds.), Biological Magnetic Resonance, vol. 8, Plenum, New York, 1989, p. 77.
[2] L. Kevan, R.N. Schwartz (Eds.), Time Domain Electron Spin Resonance, Wiley-Interscience, New York, 1979.
[3] B. Rakvin, T. Islam, I. Miyagawa, Phys. Rev. Lett. 50 (1983) 1313.
[4] B. Rakvin, Chem. Phys. Lett. 109 (1984) 280.
[5] M. Peric, B. Rakvin, A. Dulcic, J. Chem. Phys. 82 (1985) 1079.
[6] B. Rakvin, S. Valic, Z. Veksli, Chem. Phys. Lett. 182 (1991) 171.
[7] S. Valic, B. Rakvin, Z. Veksli, Z. Grubisic-Gallot, Macromolecules 23 (1990) 5182.
[8] M. Andreis, B. Rakvin, Z. Veksli, J. Polym. Sci., Polym. Phys. Ed. 25 (1987) 1709.
[9] J.T. Swann Jr., I. Miyagawa, J. Chem. Phys. 86 (1987) 1157.
[10] M. Peric, B. Rakvin, A. Dulcic, Chem. Phys. Lett. 126 (1986) 574.
[11] I. Miyagawa, K. Sogabe, S.A. Hossain, Chem. Phys. Lett. 182 (1991) 668.
[12] I. Miyagawa, K. Sogabe, M. Ohuchi, K. Hukao, Chem. Phys. Lett. 225 (1994) 364.
[13] A. Dulcic, M. Peric, J. Magn. Reson. 76 (1988) 427.
[14] A. Dulcic, B. Rakvin, J. Magn. Reson. 52 (1983) 323.
[15] M. Peric, B. Rakvin, A. Dulcic, J. Magn. Reson. 65 (1985) 215.
[16] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes, Cambridge University Press, Cambridge, 1986, p. 31.
[17] M.D. Levenson, Introduction to Nonlinear Laser Spectroscopy, Academic Press, New York, 1982, p. 14.
[18] B.T. Ghim, S.S. Eaton, G.R. Eaton, R.W. Quine, G.A. Rinard, S. Pfenninger, J. Magn. Reson. A 115 (1995) 230.
[19] T.W. Hansch, in: N. Bloembergen (Ed.), Nonlinear Optics, North-Holland, Amsterdam, 1977, p. 17.
[20] J.H. Burgess, R.M. Brown, Rev. Sci. Instrum. 23 (1951) 334.
[21] M. Peric, B.L. Bales, unpublished data.
[22] G. Sachs, W. Stocklein, B. Bail, E. Dormann, M. Schwoerer, Chem. Phys. Lett. 89 (1982) 179.
[23] H. Eichele, M. Schwoerer, Ch. Krohnke, G. Wegner, Chem. Phys. Lett. 77 (1981) 311.
[24] S.S. Eaton, G.R. Eaton, J. Magn. Reson. A 102 (1993) 354.
[25] I. Bertini, G. Martini, C. Luchinat, in: C.P. Poole, Jr., H.A. Farach (Eds.), Handbook of Electron Spin Resonance – Data Sources, Computer Technology, Relaxation, and ENDOR, AIP Press, New York, 1994, p. 51.