Journal of Magnetic Resonance 289 (2018) 26–34

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

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

Chirp echo Fourier transform EPR-detected NMR

Nino Wili, Gunnar Jeschke *

Laboratory of Physical Chemistry, ETH Zurich, Vladimir-Prelog-Weg 2, CH-8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 20 December 2017
Revised 2 February 2018
Accepted 4 February 2018
Available online 6 February 2018

Keywords:
UWB
AWG
FT EPR
ELDOR-detected NMR
Chirp pulses
2D EPR
Hyperfine spectroscopy

ABSTRACT

A new ultra-wide band (UWB) pulse EPR method is introduced for observing all nuclear frequencies of a paramagnetic center in a single shot. It is based on burning spectral holes with a high turning angle (HTA) pulse that excites forbidden transitions and subsequent detection of the hole pattern by a chirp echo. We term this method Chirp Echo Epr SpectroscopY (CHEESY)-detected NMR. The approach is a revival of FT EPR-detected NMR. It yields similar spectra and the same type of information as electron-electron double resonance (ELDOR)-detected NMR, but with a multiplex advantage. We apply CHEESY-detected NMR in Q band to nitroxides and correlate the hyperfine spectrum to the EPR spectrum by varying the frequency of the HTA pulse. Furthermore, a selective π pulse before the HTA pulse allows for detecting hyperfine sublevel correlations between transitions of one nucleus and for elucidating the coupling regime, the same information as revealed by the HYSCORE experiment. This is demonstrated on hexaaquamanganese(II). We expect that CHEESY-detected NMR is generally applicable to disordered systems and that our results further motivate the development of EPR spectrometers capable of coherent UWB excitation and detection, especially at higher fields and frequencies.

1. Introduction

Hyperfine couplings and nuclear frequencies can give detailed and valuable information about the local structure of paramagnetic centers. Sometimes these couplings can be resolved in the CW EPR spectra. If this is not the case, several different pulse EPR methods are available. The most prominent ones are ESEEM (electron spin echo envelope modulation), ENDOR (electron nuclear double resonance) and ELDOR-detected NMR (electron-electron double resonance-detected NMR, or EDNMR) [1].

EDNMR is used to measure the nuclear frequencies of paramagnetic centers employing microwave irradiation only. It was introduced more than two decades ago by Schosseler et al. [2]. This experiment is particularly useful at high fields and frequencies [3] and has recently gained popularity [4–6]. It relies on driving forbidden transitions by a very selective high turning angle (HTA) pulse whose large nominal turning angle compensates for the low transition moment. The two levels of a forbidden transition are shared with two allowed transitions that differ by the nuclear frequencies of the hyperfine doublet from the frequency of the allowed transition. Hence, a polarization change on the forbidden transition decreases the polarization of these two allowed transitions and thus their signal. The hole pattern created by the HTA pulse is measured stepwise in the frequency domain by changing the frequency difference between HTA pulse and observer sequence. This has the advantage that the holes are detected on resonance, which alleviates the dead-time problem, such that broad features can be detected. Compared to ENDOR, the resolution is usually worse, but there is no need for long radio-frequency (rf) irradiation, which prevents the application of ENDOR to centers with fast longitudinal relaxation of the electron spin. Compared to ESEEM, the resolution of EDNMR is also lower, but larger couplings are detectable and sensitivity enhancement by strongly driving the forbidden transitions is easier and more transparent than pulse matching [7].

Conceptually easier and also historically older than EDNMR is the idea of Fourier transform (FT) EPR-detected NMR [8], where the hole pattern is detected by recording an FID and a subsequent Fourier transform. The forbidden transition labelled EPR (FORTE) experiment enhances sensitivity of FT EPR-detected NMR by burning the hole with a HTA pulse and correlates the hole pattern to the EPR spectrum in a second dimension [9]. EDNMR and FT EPR-detected NMR give similar spectra and information, as they both rely on detecting a hole pattern created by a HTA pulse. However, at a given magnetic field, the spectra are different because the orientation selection affects them differently. In EDNMR, orientation selection is governed by the detection sequence, in FT EPR-detected NMR, it is governed by the HTA pulse. FT EPR-detected NMR has not become popular as it does not work well for large

* Corresponding author.
E-mail address: gjeschke@ethz.ch (G. Jeschke).

https://doi.org/10.1016/j.jmr.2018.02.001
1090-7807/

couplings and broad holes, because of the limited excitation bandwidth and severe dead time.

Both of these limitations can be overcome by the use of chirp echoes, where the frequency is swept through the spectrum during the pulse [10]. The chirp echo acquisition can be viewed as a broadband "polarization readout", which gives the complete hole pattern in one shot. In analogy to FT-NMR, this gives the direct dimension for free. The dead time problem could also be solved by a normal Hahn echo, but the bandwidth of rectangular pulses is very limited compared to chirp pulses and is insufficient for large hyperfine couplings. Several possible additional, indirect dimensions can be imagined, the most obvious one being the EPR spectrum itself. That way, the FT EPR-detected NMR spectrum can be correlated to the EPR spectrum, which gives additional information about the relative orientations of g-tensor and hyperfine coupling tensor [3].

Earlier work on the use of chirp echoes in hyperfine spectroscopy focused on ESEEM sequences [11]. In the case of single crystals, EPR spectra broader than 800 MHz in the direct dimension and nuclear frequencies up to 200 MHz in the indirect dimension could be detected. This is impossible with rectangular pulses. However, the ESEEM experiment suffers from short transverse relaxation times typical for systems with medium to large couplings, and from transverse interference effects [12]. In our hands, it did not yield satisfying spectra for disordered systems, most likely due to destructive interference from closely spaced nuclear frequencies with different phases. The problems associated with short transverse relaxation times and transverse interference are not expected for hole burning experiments.

In this work, we demonstrate the use of chirp echoes to detect the complete FT EPR-detected NMR spectrum of a nitroxide radical and the correlation to the EPR spectrum by changing the frequency of the HTA pulse step by step. The same correlation experiment is also performed on the manganese hexaquacomplex, but there the additional information is limited because of the mainly isotropic g-value and hyperfine coupling. A hyperfine sublevel correlation (HYSCORE)-type correlation experiment is introduced that is based on a polarization transfer step by a π-pulse on an allowed transition before the HTA pulse.

2. Theory

2.1. General principle of side hole burning

Polarization transfer experiments can be illustrated and discussed rather generally with the three-level system shown in Fig. 1. The states are denoted by $|i\rangle$, the corresponding population

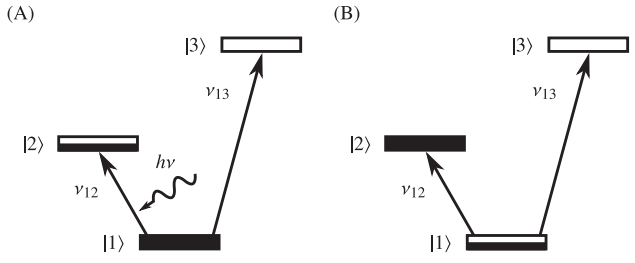

Fig. 1. Polarization transfer in systems with connected levels. (A) Before a hole burning pulse is applied. (B) After a hole burning pulse is applied. Any change of the polarization of the transition $|1\rangle \rightarrow |2\rangle$ also leads to a change in polarization of the transition $|1\rangle \rightarrow |3\rangle$. This manifests as a change in spectral intensity at an offset of $\Delta\nu = \nu_{13} - \nu_{12}$. If the spectral intensity decreases, as shown in this illustration, it is denoted hole burning. If the population of level $|2\rangle$ before the pulse is lower than the population of level $|1\rangle$, the polarization of the transition $|1\rangle \rightarrow |3\rangle$ increases, resulting in a polarization enhancement.

before a pulse is applied as $p_{i,0}$ and the population after the pulse as p_i.

In order to discuss EDNMR, we make the correspondence of observing the decreased intensity of the allowed transition $|1\rangle \rightarrow |3\rangle$ after having applied a hole burning pulse to the forbidden transition $|1\rangle \rightarrow |2\rangle$. However, the concept of hole burning is much more general. For example, in systems with zero-field splittings, a hole burning pulse is expected to increase the polarization of connected transitions. We will make no assumptions about the transition moments in the following general discussion and treat the special case of hyperfine spectroscopy in the next section. We look at spectral intensity changes of the transition $|1\rangle \rightarrow |3\rangle$. We can define a relative depth

$$d_{\text{hole}} := \frac{(p_1 - p_{1,0}) - (p_3 - p_{3,0})}{2(p_{3,0} - p_{1,0})}. \tag{1}$$

Without any perturbation, this hole depth parameter takes the value $d_{\text{hole}} = 0$. If the transition $|1\rangle \rightarrow |3\rangle$ is saturated, then $p_1 = p_3 = (p_{2,0} + p_{3,0})/2$ and $d_{\text{hole}} = 1/2$. Finally, if the transition $|1\rangle \rightarrow |3\rangle$ is inverted, then $p_3 = p_{1,0}$ and $p_1 = p_{3,0}$ which leads to $d_{\text{hole}} = 1$. $d_{\text{hole}} < 0$ corresponds to polarization enhancement.

If we assume that a (hole burning) pulse is applied to transition $|1\rangle \rightarrow |2\rangle$, then level $|3\rangle$ is untouched. Still, the intensity of the observed transition $|1\rangle \rightarrow |3\rangle$ at an offset of $\Delta\nu = \nu_{13} - \nu_{12}$ with respect to the hole burning pulse changes. Since $p_3 = p_{3,0}$, it follows that

$$d_{\text{hole}} = \frac{p_1 - p_{1,0}}{2(p_{3,0} - p_{1,0})} = \frac{p_1 - p_{1,0}}{-2(\Delta_0 p_{13})} \tag{2}$$

with the initial polarization $\Delta_0 p_{13} = p_{1,0} - p_{3,0}$ on transition $|1\rangle \rightarrow |3\rangle$.

For a given microwave strength B_1 we can define a nominal flip angle for the hole burning pulse [9].

$$\beta_0 = \frac{g_e \beta_e}{\hbar} B_1 \cdot t_p = \omega_1 \cdot t_p, \tag{3}$$

with the electron g-factor g_e, the Bohr magneton β_e, the reduced Planck constant $\hbar$, the pulse length t_p and $\omega_1 = g_e \beta_e B_1/\hbar$. Since different transitions can have different transition moments μ, it is sensible to define an effective flip angle per transition $|i\rangle \rightarrow |j\rangle$

$$\beta_{ij} = \mu_{ij} \beta_0. \tag{4}$$

If $|i\rangle \rightarrow |j\rangle$ is a forbidden transition, μ_{ij} is very small, and a high nominal turning angle is needed to achieve a significant change in populations.

We can now express p_2 and d_{hole} as a function of the effective flip angle of the hole burning pulse

$$p_2 = \frac{1}{2}\left[p_{2,0} \cdot (1 + \cos\beta_{12}) + p_{1,0} \cdot (1 - \cos\beta_{12})\right]$$

$$p_2 - p_{2,0} = \frac{1}{2}\left[p_{2,0} \cdot (\cos\beta_{12} - 1) + p_{1,0} \cdot (1 - \cos\beta_{12})\right]$$

$$= \frac{\Delta_0 p_{12}}{2}\left[1 - \cos(\mu_{12}\beta_0)\right]$$

which yields

$$d_{\text{hole}} = -\frac{\Delta_0 p_{12}}{4\Delta_0 p_{13}}\left[1 - \cos(\mu_{12}\beta_0)\right]. \tag{5}$$

We can identify the inversion factor

$$f_{\text{inv}} = \frac{1}{2}\left[1 - \cos(\mu_{12}\beta_0)\right] \tag{6}$$

which is 0 before hole burning, 1/2 for saturation, corresponding to an effective flip angle of $\pi/2$, and 1 for inversion. This simplified