

# Application of High Frequency EPR to Integer Spin Systems: Unusual Behavior of the Double-Quantum Line

Pieter J. van Dam, Adri A. K. Klaassen, Eduard J. Reijerse, and Wilfred R. Hagen

*Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

E-mail: hagen@sci.kun.nl

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**A high-frequency EPR study is presented of the integer spin system Ni(II) in the host of Zn-tris(ethylenediamine) dinitrate. This complex shows a broad structureless line at X band. At D band (130 GHz) however, a standard triplet powder spectrum is observed. Superimposed on this spectrum is a “double-quantum” line at the expected position. The microwave power dependency of this line is found to be in contradiction with existing theory on multiple-quantum transitions. The line in our spectra shows a single quantum line behavior in intensity and linewidth as a function of the microwave frequency from 35 to 130 GHz. A literature survey leads to the conclusion that most double-quantum features in high-spin systems do not follow the  $P^{3/2}$  power dependency predicted by second-order perturbation theory. In our case the double-quantum line is assigned to an enhancement effect due to the simultaneous excitation of two single-quantum transitions.** © 1998 Academic Press

**Key Words:** high-frequency EPR; triplet; double-quantum transition; high-spin system.

High-frequency EPR spectrometers ( $\nu \geq 95$  GHz) have been developed in several laboratories worldwide (1–4). In comparison with conventional EPR spectrometers (X band, 9 GHz and Q band, 35 GHz) these spectrometers provide increased resolution of the  $g$  tensor of  $S = \frac{1}{2}$  systems (5, 6) or high-resolution ENDOR (7). Until now few investigations have demonstrated the usefulness of these spectrometers for high-spin systems with large zero field splitting (ZFS) parameters, which cannot be studied with conventional low-frequency EPR (8, 9). We have used multifrequency EPR to study an integer spin system of Ni(II). Triplet powder spectra of nitrogen-coordinated Ni(II) compounds have been described by Reedijk *et al.* (10). For those systems with ZFS parameters of intermediate magnitude only incomplete spectra at Q band were obtained. To demonstrate the usefulness of high-frequency EPR in the case of large zero-field splittings we studied the complex of Ni(II) doped into a host of  $[\text{Zn}(\text{en})_3](\text{NO}_3)_2$  (11, 12).

$\text{Ni}^{2+}$  cations are part of biological systems, for instance, the Ni(II) tetrapyrrole cofactor  $\text{F}_{430}$  in methyl coenzyme M reductase. The six-coordinated Ni(II) of the cofactor has spin

$S = 1$  but is EPR silent at conventional frequencies (13) due to the large ZFS. High-frequency EPR would be a useful tool to accurately measure the ZFS parameters of this system. As a spectroscopic model complex for these type of nickel systems we have studied a powder of Ni(II)-doped zinc-tris-(ethylenediamine)dinitrate,  $[\text{Zn}(\text{en})_3](\text{NO}_3)_2$ . We have detected a strong “double-quantum” line in the powder triplet spectra of this Ni(II) complex at a frequency of 130 GHz. The unusual behavior of this line is compared to data available in the EPR literature on double-quantum transitions.

Purple crystals of Ni(II) doped into  $\text{Zn}(\text{en})_3(\text{NO}_3)_2$  were grown as described by Sreeramachandra Prasad and Subramanian (11) with a nickel concentration of 4%. Crystals were crushed to a finely divided powder in order to simulate a frozen solution, and put into quartz capillaries (o.d. 0.6 mm, i.d. 0.4 mm).

The high-frequency EPR spectrometer is based on a free running fixed frequency source in combination with a frequency tunable single-mode cylindrical resonator ( $\text{TE}_{011}$ ). Millimeter waves are generated using higher harmonics of a dielectric resonator stabilized transistor oscillator at 8 GHz. These 130-GHz harmonics were further amplified via an injection-locked IMPATT amplifier. A Bolometer (InSb) immersed in liquid helium was used as microwave detector. A wide-bore (60-mm) resistive Bitter magnet of the High Field Magnet Laboratory in Nijmegen that is capable of generating fields up to 15 T was used for the magnetic field (14). This type of magnet makes it possible to sweep the full field range in a few minutes. Field modulation and phase-sensitive detection was applied at 20 kHz using a digital lock-in amplifier (SRS 830) and a Quad 303 audio amplifier.

For a basic triplet system without hyperfine interaction the spin Hamiltonian is given by

$$\mathcal{H}_{\text{sp}} = \beta \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2), \quad [1]$$

in which  $D$  and  $E$  determine the principal elements of the traceless zero field tensor ( $X = D/3 + E$ ,  $Y = D/3 - E$ ,

$Z = -2D/3$ ). The spectra of randomly oriented triplet systems have been described extensively (15–17), and are basically determined by the powder pattern of the single-quantum  $\Delta m_s = 1$  transitions, the single-quantum  $\Delta m_s = 2$  line, also called  $H_{\min}$  line or half-field line and the double-quantum  $\Delta m_s = 1 + 1$  line. For this double-quantum line an intermediate level is required and thus the triplet levels must be at equidistant separation.

Simulations of the powder patterns of triplet spectra have been included in our work. These simulations were constructed as follows. A program was written for  $S = 1$  along the lines outlined in the classical paper by Wasserman *et al.* (15). The procedure involves exact diagonalization of the energy matrix that corresponds to the Hamiltonian of Eq. [1] for an increasingly refined grid of  $B_0$  values until the resonance condition is met for a given pair of energy levels  $h\nu = \Delta E$ . The new state vectors are calculated and from these the transition probability. Finally, a symmetric Gaussian in magnetic-field units (truncated at 0.1% intensity) is convolved with the stick position of the resonance. We have previously used this approach to simulate  $S = 2$  powder patterns (18). The present program also affords the powder pattern of the double-quantum transition by the following procedure. For each molecular orientation the calculated Gaussian for the two regular  $\Delta m = 1$  transitions (in high-field notation  $|+1\rangle$ ,  $|0\rangle$  and  $|0\rangle$ ,  $|-1\rangle$ ) are compared. Whenever the two truncated Gaussians have a finite overlap their product is stored separately as the intensity of the double-quantum transition except for an overall scaling factor. Once the two powder patterns for the regular spectrum and for the double-quantum spectrum have been generated the scaling factor is determined by adjusting their sum to fit the experimental amplitudes.

Apart from the transition probability, the intensity of the double-quantum line is also determined by its spectral density, i.e., the number of orientations where the condition of equidistant levels is fulfilled.

Analytical solutions for the nuclear quadrupole resonance ( $I = 1$ ) eigenvalue problem have already been derived by Muha (19). These formulas have been adapted for electronic triplet systems, replacing the nuclear quadrupole parameters  $K$  and  $\eta$  by the ZFS parameters  $D$  and  $E$  ( $K = D/3$ ,  $\eta = 3E/D$ ). If we include the condition that the two transitions have the same energy difference, i.e., are excited at the same moment, the solution for the orientations ( $\theta$ ,  $\phi$ ) is

$$\begin{aligned} \cos^2\theta + \cos 2\theta + \frac{3E}{D} \sin^2\theta \cos 2\phi \\ = \frac{2D^2}{9} \left(1 - \left(\frac{3E}{D}\right)^2\right) \left(\frac{1}{g\beta B}\right)^2. \end{aligned} \quad [2]$$

In the absence of rhombicity ( $E = 0$ ) this equation simplifies to

$$3 \cos^2\theta - 1 = \frac{2D^2}{9(g\beta B)^2}. \quad [3]$$

The number of orientations that have equidistant levels is proportional to  $\sin \theta$ , and thus the intensity of the double-quantum line ( $I_{dq}$ ) is proportional to

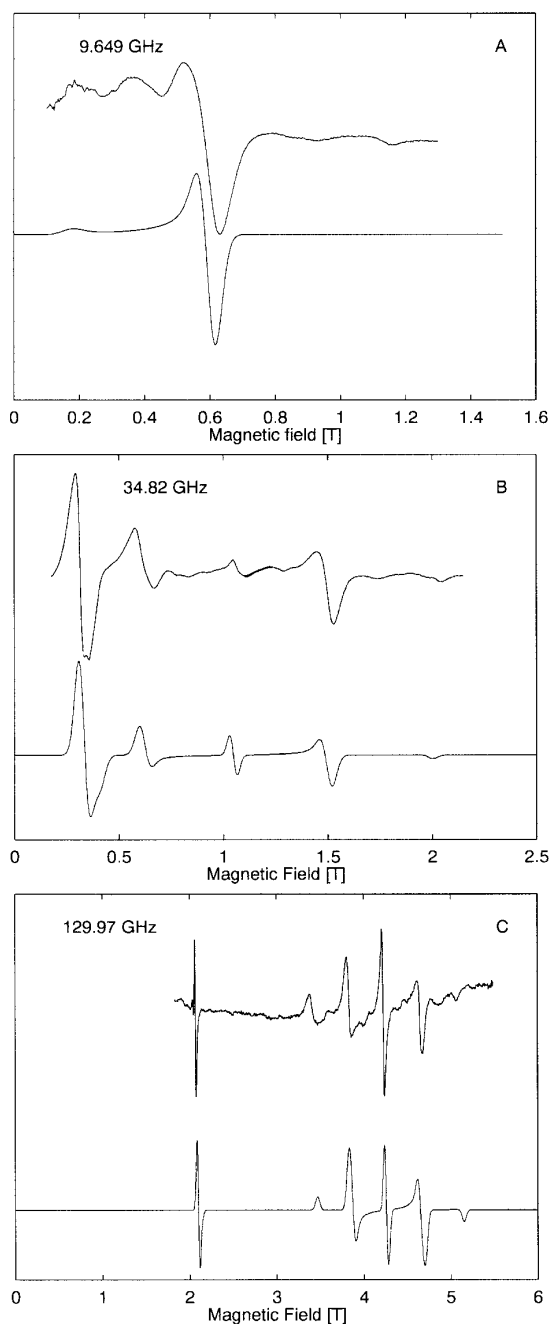
$$I_{dq} \propto \sqrt{1 - \left(\frac{D}{3g\beta B}\right)^2}. \quad [4]$$

For large magnetic fields ( $g\beta B \gg D$ ) the maximum number of orientations that contribute to the double-quantum line will occur at the magic angle  $\theta = 54.7^\circ$  with respect to the molecular  $z$  axis.

A previous single-crystal Q-band EPR study of  $[\text{Ni:Zn(en)}_3](\text{NO}_3)_2$  has yielded the zero-field parameters ( $D = -0.832 \text{ cm}^{-1}$ ,  $E = 0 \text{ cm}^{-1}$  with  $g_x = g_y = 2.156$ ,  $g_z = 2.181$ ) at room temperature (12). Sreeramachandra Prasad and Subramanian (11) reported a larger isotropic  $g$  value of 2.20 but our powder spectra, below, are in agreement with the values from Wilson *et al.* (12). At low temperature, 146 K, a phase transition introduces a rhombic distortion of the site.

Conventional X band EPR only yielded a broad unresolved feature at 0.6 T (Fig. 1A). At 35 GHz,  $h\nu$  is approximately equal to the zero field splitting parameter  $D$ , and a complete triplet powder pattern is observed but part of the  $\Delta m = 1$  transitions are obscured by the  $\Delta m = 2$  or  $H_{\min}$  transition (Fig. 1B). At 1.1 T, a weak  $\Delta m_s = 1 + 1$  or double-quantum line is visible. At 130 GHz the whole triplet spectrum is well separated from the  $\Delta m_s = 2$  line, and the double-quantum line has grown to the most prominent feature of the spectrum (Fig. 1C). Simulations with the ZFS parameters  $D = 0.832 \text{ cm}^{-1}$ ,  $E = 0 \text{ cm}^{-1}$ , and  $g_x = g_y = 2.156$ ,  $g_z = 2.181$  (12) are included and reproduce the spectra well. All simulations were done with a frequency-independent linewidth of 30 mT. Only the linewidth of the  $H_{\min}$  line at 130 GHz is considerably smaller at high frequency compared to the low frequency spectra.

According to theory the double-quantum line is from a second-order process, and thus the transition probability will be proportional to  $B_1^4$  (17, 20). The intensity of the line is thus proportional to  $P^{3/2}$  ( $P$  is the incident microwave power in milliwatts) and should only be observable at high microwave powers. We have studied the microwave power dependency of the triplet lines at 35 and 130 GHz as shown in Fig. 2. Over the two frequencies the ratio between the intensities of the single-quantum and double-quantum lines remained constant. For single-quantum lines the intensity of the line is linear with the square root of the microwave power, therefore,  $\Delta \log I / \Delta \log P = 0.5$ . For the double-quantum lines an intensity over microwave power ratio of 1.5 is expected. Contrary to expectation double log plots of the intensity as a function of the microwave power reveals that the intensity of the double-quantum line is proportional with  $P^{1/2}$  as is the case for the single-quantum lines.

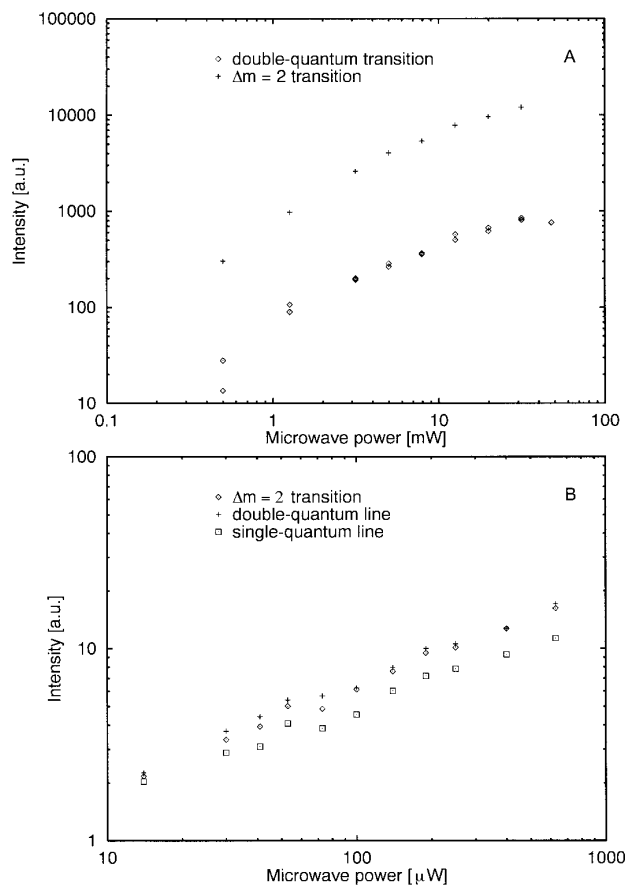


**FIG. 1.** X band (A), Q band (B), and D band (C) room temperature EPR spectra of Ni(II) in  $[\text{Zn}(\text{en})_3](\text{NO}_3)_2$ . Experimental conditions were as follows. X band: microwave power, 15 mW; modulation amplitude, 0.5 mT; modulation frequency, 100 kHz. Q band: microwave power, 30 mW; modulation amplitude, 0.5 mT; modulation frequency, 100 kHz. D band: microwave power, 0.2 mW; modulation amplitude, 0.6 mT; modulation frequency, 20 kHz. The lower traces are simulations as described in the text using the parameters from Wilson *et al.* (12) ( $D = 0.832 \text{ cm}^{-1}$ ,  $E = 0 \text{ cm}^{-1}$ , and  $g_x = 2.156$ ,  $g_y = 2.156$ ,  $g_z = 2.181$ ).

Several authors have described the presence of double-quantum and multi-quantum transitions in EPR spectra of high-spin systems, namely, biradicals (17, 21, 22) and tran-

sition metals  $\text{Ni}^{2+}$  (23, 24),  $\text{Fe}^{2+}$  (25, 26), and  $\text{Mn}^{2+}$  (27, 28). Some authors report the intensity of this double-quantum line as a function of the microwave power or give a qualitative indication of the power dependency. These literature data are summarized in Table 1. Some authors found the expected ratio of 1.5 between the  $\Delta \log I_{\text{dq}}$  and  $\Delta \log P$  while others found significantly larger ratios. Some caution must be used in comparing these data because the type of detector has not always been specified. However, all authors report a stronger dependency for the double-quantum transition on the microwave power compared to that for the single-quantum line. Also, the double-quantum line is only detected at high microwave power, and the linewidth of the double-quantum line is much smaller than that of the single-quantum line. From the overview in Table 1 it is also clear that the reported behavior of the double-quantum line is usually not according to theory; therefore, more attention should be paid to the microwave power dependency of this line.

In the present case, however, the double-quantum line remains detectable even at very low microwave power, and



**FIG. 2.** A double log plot of the intensity of the EPR lines (measured as the peak-to-peak height in the derivative spectrum) as a function of the microwave power: (A) Q band spectra and (B) D band spectra.

**TABLE 1**  
**The Microwave Power Dependency of the "Double-Quantum" Transition as Reported in the Literature for Biradicals and Transition Metals**

Compound (Reference)	$T$ (K)	$\nu$ (GHz)	$\frac{\Delta \log I_{dq}}{\Delta \log P}$	$\frac{\Delta \log I_{sq}}{\Delta \log P}$
Phenantrene (17)	77	9.28	1.5	
Acetyl-D,L-alanine ( $\gamma$ irr.) (21)	RT	9	2.4	0.4
Bis(tetraglyme)rubidiumbiphenyl (22)	7	9.4	3.1	0.5
Mn <sup>2+</sup> in MgO (27)	77		1.5	0.5
	136	9.4	3	
Ni <sup>2+</sup> in MgO (24)	126	9.4	3	
<sup>61</sup> Ni <sup>2+</sup> in MgO (29)	77	9.2	2	1
Mn <sup>2+</sup> in CaO (28)	300	9.76	1.5	
Ni <sup>2+</sup> in [Zn(en) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> (this work)	RT	34.8	0.5	0.5
	RT	129.97	0.5	0.5

*Note.* Experimental conditions that were specified have been included. If one digit for the ratio is listed, only a qualitative indication was given (linear, square-dependence) while with two significant digits the ratio was derived from a intensity versus power plot.

the linewidth of the double-quantum line is on the same order as that of the single-quantum lines. Since the double-quantum line in our spectra behaves in all aspects like a single-quantum line (i.e., both in microwave power dependency and linewidth) we have come to the conclusion that we are observing an enhanced single-quantum line instead of the double-quantum line expected at this position. This enhancement might be the result of simultaneous excitation of both single-quantum transitions leading to a greater population difference between levels. The enhancement of this  $\Delta m = 1 + 1$  line is further multiplied by the number of contributing orientations, dependent on the ratio  $g\beta B/D$  of Eq. [4], and this explains the strong intensity at 130 GHz as compared to spectra measured at lower frequencies. It cannot be excluded that at higher microwave power a real, much sharper double-quantum line would appear at the same field position. To gain more insight into the nature of the observed pseudo double-quantum line, temperature-dependent experiments on several triplet systems are planned.

Being a prominent sharp feature of the triplet spectrum this  $\Delta m = 1 + 1$  line will be useful in the case of less resolved triplet spectra from samples of low concentration or with larger ZFS parameters, like, for instance, biological systems. In such cases the single-quantum features will become less resolved or even disappear completely. The  $H_{\min}$  and double-quantum line will then be the sole sharp features available to detect the triplet spectra and to obtain the ZFS parameters.

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