

## DPPH as a Standard for High-Field EPR

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The potential utility of DPPH as a standard sample for high-field EPR (electron paramagnetic resonance) is discussed. CW-EPR spectra of solid and dissolved DPPH samples were measured using a high-field, broadband spectrometer in the frequency range 109 to 465 GHz. A single exchange-narrowed line with no apparent structure was observed for solid polycrystalline samples within the whole range. The solution spectra revealed a broader spectrum with a characteristic quintet due to the partly resolved hyperfine  $^{14}\text{N}$  structure. The overall shape and width of the high-field signals are similar to the well-known results obtained from conventional experiments which leads us to a conclusion that DPPH can be used as a standard for high-field EPR, at least for measurements up to 17 T (0.5 THz).

The growing popularity of high-field electron paramagnetic resonance spectroscopy has brought attention back to the problem of a suitable standard for calibrating the magnetic field and determining the  $g$  factor of the spin species under study. This problem is of even more importance in high-field than in conventional EPR since (i) there are no commercial gaussmeters available to measure the field above a few tesla and the field is usually determined from the magnet current, and (ii) the settability of superconducting magnets operating at high fields leaves some margin for error which can be significant in high-resolution EPR spectroscopy.

One of the most widely used standards in conventional EPR spectroscopy is 2,2-diphenyl-1-picrylhydrazyl (DPPH). This radical is well characterized at low fields and frequencies. The room-temperature EPR spectrum of polycrystalline DPPH at X band consists of a single narrow line appearing at  $g = 2.0036 \pm 0.0002$  ( $I$ ).

The small width of the Lorentzian-like single line appearing in solid DPPH is due to exchange narrowing and varies from 0.15 to 0.81 mT depending on the solvent from which it was precipitated ( $1, 2$ ). In solution, depending on its concentration, the extreme-narrowing mechanism is partly or totally suppressed, and a hyperfine quintet from two nitrogen nuclei is observed. Further dilution and degassing leads to resolving small couplings from the several hydrogen nuclei present in the molecule. In both phases, solid

and dissolved, DPPH is reasonably stable in the air at ordinary temperatures, and under certain limitations can be employed as a convenient intensity and  $g$ -factor standard ( $2$ ).

It appears logical to use this standard in high-field EPR studies, too, and it has in fact been done, for example, as reported in the series of papers by Motokawa and co-workers ( $3$ ). However, those studies were low-resolution experiments performed in a rapidly swept magnetic field generated by pulsed magnets, and the problem of DPPH lineshape and width was not relevant. On the other hand, the suitability of DPPH for high-resolution, high-field EPR spectroscopy was questioned by Lynch *et al.* in the description of their high-frequency (250 GHz) spectrometer ( $4$ ). In particular, the published spectrum of polycrystalline DPPH was broad (4.8 mT) and structured. The signal width and shape were explained by the  $g$ -factor anisotropy becoming prominent at high fields. This was recently confirmed by the same research group at a somewhat lower Larmor frequency of 170 GHz ( $5$ ). A similar result was also previously obtained by one of us ( $6$ ) and confirmed in private communications by other researchers from the high-field EPR community. It followed that DPPH was not a suitable standard for high-resolution, high-frequency EPR.

The availability of a multifrequency, high-field EPR spectrometer at the NHMFL has prompted us to search for a proper calibration standard at high frequencies. We included DPPH in that search despite the negative results summarized above. Specifically, we were concerned whether its EPR signal remains a single, symmetric line under those conditions and what linewidth it exhibits. If it behaved as in conventional EPR spectroscopy, DPPH could be employed as a standard in high fields as well. If, on the other hand, the observations reported in ( $4$ – $6$ ) were confirmed, the search should continue for a suitable standard that would produce a narrow, single line in fields up to at least 17 T.

One milligram of DPPH (Sigma) was carefully ground in an agate mortar and formed into a thin, evenly distributed layer that filled the whole surface of the bottom lid of a cup-shaped Teflon holder (6 mm i.d.). The holder was placed in the transmission-type probe of our high-field EPR spectrometer, which will be described in more detail in a forth-

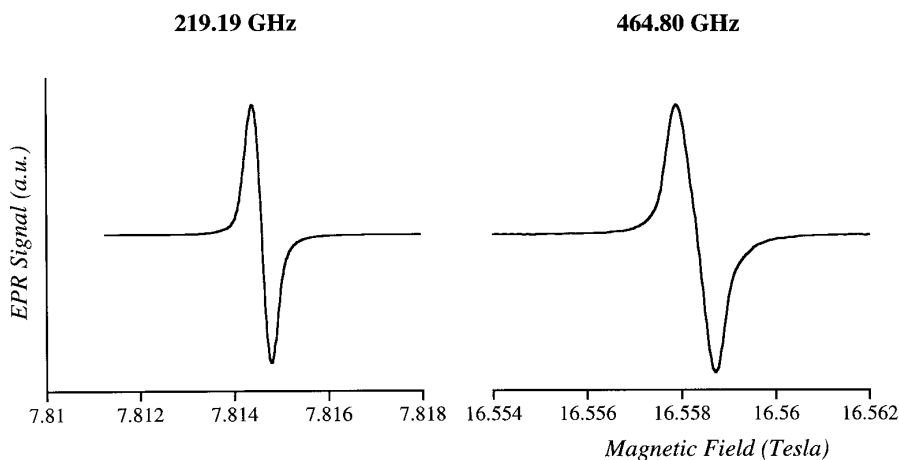


FIG. 1. Room-temperature EPR spectra of polycrystalline DPPH at two different Larmor frequencies.

coming paper (7). The system operates in a frequency range 30 GHz–3 THz using several millimeter- and submillimeter-wave sources, at fields ranging from 0 to 17.1 T. For the purpose of this work, we used two Gunn oscillators as sources, one operating at  $95 \pm 3$  GHz, the other at  $110 \pm 3$  GHz (AB Millimetre, Paris). Each of them is equipped with a set of Schottky diode harmonic generators and high-pass filters (AB Millimetre), making it possible to work also at higher harmonics of those frequencies. The fundamental frequency is measured with an EIP578B counter. The magnet (Oxford Instruments Teslatron) consists of a main set of superconducting coils which can be put in a persistent mode in the vicinity of resonance and a smaller superconducting sweep coil operating in a nonpersistent mode and allowing sweep of the field over  $\pm 0.1$  T with respect to the main coils. For fields higher than 14.5 T, the magnet temperature needs to be lowered to 2.2 K using a lambda plate. The magnetic field homogeneity was checked by NMR to be better than  $10^{-5}$  in a 1 cm sphere throughout the whole field range.

The Larmor frequencies selected were approximately 109, 219, 326, 372, 436, and 465 GHz. Figure 1 presents the spectra at 219 and 465 GHz, the former being chosen since it was the closest to the published high-resolution, high-field EPR spectra of DPPH (4) and the latter since it was as high as our combination of submillimeter-wave sources and magnetic field allowed us to proceed. In the entire frequency range, the EPR spectrum of DPPH powder consists of a single, almost symmetrical signal. The linewidth increases with the frequency: at 219 GHz, it is approximately 0.39 mT while at 465 GHz it reaches 0.85 mT. Only at the highest frequencies (above 400 GHz) does the signal show the first signs of being of composite nature, but it still remains an unresolved, single line. The slight asymmetry may be attributed to some admixture of dispersion into the absorption signal, which is unavoidable in a spectrometer of current

simple configuration. The frequency dependence of linewidth is presented in Fig. 2, which also contains the results of X- and Q-band measurements independently performed using conventional spectrometers on the same sample we studied at high frequencies. The linewidth at X band was 0.16 mT while at Q band it decreased to 0.108 mT.

Since DPPH is often used as a standard in solution, we also recorded EPR spectra of a 0.6 mM solution of DPPH in toluene at approximately 218 and 326 GHz. Figure 3 presents the spectrum at 326 GHz. The solution spectrum is broader than in the solid state and reveals a single line with a superimposed characteristic quintet resulting from the partly resolved hyperfine structure due to an interaction of the unpaired electron with the two  $^{14}\text{N}$  nuclei. We did not try to improve the resolution by degassing and/or diluting the solution.

The most fundamental observation is that of a presence of only one, single, unstructured, and reasonably symmetri-

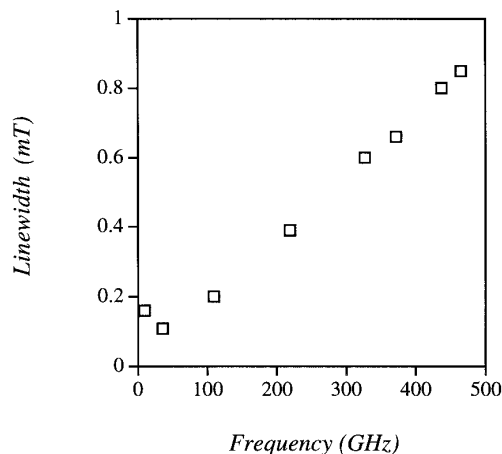
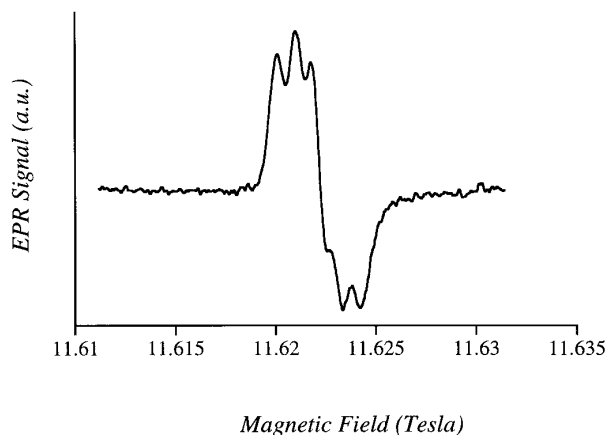


FIG. 2. Larmor frequency dependence of polycrystalline DPPH EPR linewidth at room temperature.



**FIG. 3.** EPR spectrum of 0.6 mM solution of DPPH in toluene at 326 GHz.

cal EPR signal in the DPPH room-temperature spectrum throughout the whole frequency range under study (109–465 GHz). We find no obvious explanation of the discrepancy between this observation and the previous published or unpublished results reporting complex and structured spectra of DPPH. One possible reason could be the difference in composition between DPPH samples. As discussed first in Ref. (1) and later more comprehensively in Ref. (2), DPPH from different batches exhibits varying linewidth in X-band EPR. This is mainly attributed to a different number of solvent molecules contained in the crystal structure. The narrowest linewidth (0.15 mT) is exhibited by DPPH recrystallized from carbon disulfide, and such a sample is considered to contain no solvent in its lattice. Samples recrystallized from other solvents may produce linewidths of 0.8 mT and more at X band.

Let us remark here that our sample with its linewidth of 0.16 mT as measured in X band was among the narrowest measured at that frequency, while that reported on in Ref. (4) exhibited a significantly larger linewidth of 0.24 mT at X band. It is conceivable that such differences may be magnified by the power of high-field EPR resolution, particularly since the presence of solvent molecules in the crystal lattice should have an effect on dipolar broadening taking place in the crystal (see below). The information on the solvent from which DPPH was crystallized is seldom supplied by commercial vendors. Also, there appears some confusion regarding the meaning of the ‘‘DPPH’’ acronym: while Sigma offers 2,2-diphenyl-1-picrylhydrazyl as DPPH, Aldrich markets another compound, 2,2-di(4-*tert*-octylphenyl)-1-picrylhydrazyl, under the same name. Additionally, we may remark that although 2,2-diphenyl-1-picrylhydrazyl is generally considered chemically stable in solid state, Ref. (2) quotes examples for which it should not always be assumed to be true. In any case, the result presented in this paper should be considered as a benchmark for further studies, and

DPPH producing broad, structured spectra at frequencies up to 465 GHz should be treated as of uncertain composition or quality.

The observed dependence of EPR linewidth on Larmor frequency requires the following consideration. The linewidth of magnetically nondiluted solids is determined by the competition between broadening effects and exchange narrowing (8–12). Among other possible processes, dipolar broadening is expected to be the main cause of broadening in our sample (11). Dipolar broadening is usually described in terms of the second moment which is written as the sum of three contributions (13, 14), the first one, usually called secular, being

$$M_2 = \frac{3}{4} S(S+1) \mu_B^2 g^2 \sum (1 - \cos^2 \theta_{jk})^2 / r_{jk}^6, \quad [1]$$

where  $r_{jk}$  is the modulus of the vector joining the  $j$ th spin to the  $k$ th spin and  $\theta_{jk}$  is the angle between this vector and the direction of the static magnetic field. The second moment is easily calculated following Eq. [1] if one knows the details of the crystal structure. The exchange-narrowed linewidth is then given by  $\Delta B_{pp} = M_2 / J_{ex}$  (10), where  $J_{ex}$  is the exchange coupling constant in magnetic field units. This approximation is valid when the Zeeman term is larger than the exchange term. In this ‘‘weak exchange’’ limit, the linewidth is frequency independent. Frequency dependence of the linewidth is introduced for higher exchange rate and/or lower Larmor frequency, where the wings of the satellite lines at frequencies 0,  $2\mu_B g/h$ , and  $3\mu_B g/h$  contribute to the second moment of the line at the Larmor frequency  $\mu_B g/h$  (8, 14–16). In such a case, the resulting line is broader than that calculated with Eq. [1] by a factor of 10/3 (10).

An expression for the frequency dependence of the linewidth is given by Kubo and Tomita (16) as

$$\Delta B_{pp} = \frac{M_2}{J_{ex}} \left\{ 1 + \frac{5}{3} \exp \left[ -\frac{1}{2} \left( \frac{\omega_0}{\omega_{ex}} \right)^2 \right] + \frac{2}{3} \exp \left[ -2 \left( \frac{\omega_0}{\omega_{ex}} \right)^2 \right] \right\}, \quad [2]$$

where  $\omega_0$  and  $\omega_{ex}$  are the Larmor and the exchange frequencies, respectively, and  $M_2$  is the secular term of the dipolar second moment as calculated with Eq. [1]. According to this expression, for large exchange frequencies, i.e.,  $\omega_0/\omega_{ex} \rightarrow 0$ , the sum of the two exponentials in Eq. [2] approaches 7/3 and thus  $\Delta B_{pp} = 10M_2/3J_{ex}$ . For large values of  $\omega_0/\omega_{ex}$ , the two exponentials are negligibly small, and the linewidth approaches the frequency-independent limit  $\Delta B_{pp} = M_2/J_{ex}$ . In the intermediate region, the linewidth is frequency dependent. In particular, for a constant exchange rate, narrowing is expected with increasing Larmor frequency and was indeed

experimentally observed (17, 18). This is exactly what happens in our experiment between the X band and the Q band and tells us that in that frequency range we are in a regime where  $\omega_{\text{ex}}$  is equal or greater than  $\omega_0$ .

In order to better estimate the exchange frequency, we ran a sample calculation using the point-dipole approximation and assuming first that the electron is equally shared between the two nitrogen atoms,  $N_\alpha$  and  $N_\beta$ . The same calculation was then repeated assuming electron delocalization over the aromatic rings as determined by polarized neutron diffraction (19), EPR (20, 21), and ENDOR (21) data. In the first case, the calculated second moment  $M_2$  was 166.02  $\text{mT}^2$  and in the second case it was 749.79  $\text{mT}^2$ . These two results produce upper and lower limits of the dipolar broadened linewidth as  $\Delta B_{\text{pp}} = 12.9$  and 27.4 mT, respectively. Using Eq. [2] and the experimentally determined values of  $\Delta B_{\text{pp}}$  at X and Q bands, we estimated the exchange energy to be in the range 3–4  $\text{cm}^{-1}$  for the first calculation and 15–20  $\text{cm}^{-1}$  for the second. Most probably it is contained between those two limits.

A full numerical analysis is beyond the scope of this paper; however, at this level of analysis the following conclusions can be drawn: (i) The frequency dependence of the linewidth in the low-frequency range (X and Q bands) qualitatively agrees with the model of exchange narrowing for the case of intermediate exchange. (ii) Although a thorough quantitative treatment would require a study of a single crystal, we were able to estimate the order of magnitude of exchange and dipolar interactions in DPPH from the powder spectra and explain the low-frequency behavior of the linewidth. (iii) According to the exchange narrowing theory, our observation of broadening with increased Larmor frequency is an unexpected result. A trivial explanation would be an instrumental effect like an existence of a field gradient over the sample volume which would increase with field. However, we have extensively tested our field homogeneity using  $^1\text{H}$  (for low fields) and  $^2\text{D}$  (for high fields) NMR, and we found that at linewidth on the order of 0.2 mT we were at least one order of magnitude away from any homogeneity problems. We can thus tentatively attribute the observed effects to (a)  $g$ -factor anisotropy, (b)  $g$  strain, (c) frequency dependence of the relaxation time  $T_2$ , or to a combination of all these factors. The last point is clearly the most interesting one and deserves further investigation.

Regarding the influence of  $g$ -factor anisotropy, we performed simulations for a spin doublet with an axial  $g$ -factor anisotropy of  $\Delta g = 0.0001$ , which showed a broadening similar to that observed in our spectra between 109 and 465 GHz, without resolving the two  $g$  components only assuming a simultaneous broadening of the intrinsic linewidth from 0.1 to 0.15 mT. This is in agreement with the idea of a combination of  $g$ -factor anisotropy and frequency-dependent relaxation as the basis for the observed behavior.

The isotropic hyperfine splitting observed in solution

spectra is on the order of 0.94 mT and similar to that obtained from the X-band experiments (19, 20). As expected in a solution spectrum, the  $g$ -factor anisotropy remains averaged out by the Brownian motions and molecular tumbling.

In general, the striking feature of our spectra, both in the solid state and in solution, is that they are very similar to those known from X-band EPR, small linewidth differences in solids notwithstanding. This suggests that DPPH may serve as a standard also in high-field spectroscopy. In fact, Fig. 1 illustrates well the usefulness of this standard: in both spectra, the magnetic field is calculated from the nonpersistent sweep coil current added to the persistent current in the main coil. Assuming that the  $g$  factor of the DPPH does not change with frequency—and we have found no physical phenomenon which would give reason to that—we find out that while at 219 GHz the field was calculated accurately from the magnet current, at 465 GHz we were off from the true field value by 5 mT. This phenomenon is due either to mutual coupling of superconducting coils being parts of the magnet, or to errors by the power supplies, or both, and is to be expected while working at very high fields generated by superconducting magnets consisting of multiple coils.

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*Note Added in Proof.* Since the submittal of this Communication, we have performed EPR experiments at 110 and 330 GHz on 2,2-di-(4-tert-octylphenyl)-1-picrylhydrazyl (Aldrich). The resulting spectra showing a pronounced  $g$ -factor anisotropy ( $\Delta g = 0.0016$ ) confirm that the principal reason for the discrepancies existing between different "DPPH" samples and discussed in the article is indeed their chemical composition.

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