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Temperature Dependence of Electron Spin Relaxation of 2,2-diphenyl-1-picrylhydrazyl in Polystyrene

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Abstract

The electron spin relaxation rates for the stable radical DPPH (2,2-diphenyl-1-picrylhydrazyl) doped into polystyrene were studied by inversion recovery and electron spin echo at X-band and Q-band between 20 and 295 K. At low concentration (340 μM , 0.01%) spin-lattice relaxation was dominated by the Raman process and a local mode. At high concentration (140 mM, 5%) relaxation is orders of magnitude faster than at the lower concentration, and $1/T_1$ is approximately linearly dependent on temperature. Spin lattice relaxation rates are similar at X-band and Q-band. The temperature dependence of spin echo dephasing was faster at about 140 K than at higher or lower temperatures, which is attributed to a wagging motion of the phenyl groups.

1. Introduction

DPPH (2,2-diphenyl-1-picrylhydrazyl, Fig. 1) is a solid stable radical with various applications in EPR and NMR. The well-characterized spectrum of crystalline DPPH has been used as a standard for g-factor determination [1] and for spectrometer performance evaluation [2]. In solution, DPPH has been used as a radical scavenger for kinetics measurements and to probe radical efficiencies [3] and for dynamic nuclear polarization (DNP) to enhance NMR signals [4]. Although it is one of the most extensively studied radicals in EPR, its electron spin relaxation times have been studied predominantly for samples with high concentrations, in the range of 3 to 140 mM, as is typical for DNP experiments. T_1 for DPPH doped into solid matrices is concentration dependent [5–7], and the relaxation rate has been reported to be inversely proportional to the square of the concentration [8]. Prior measurements of T_1 for DPPH dissolved in polymers were performed using saturation recovery [6] and progressive saturation methods [5, 7–9]. It was observed that $1/T_1$ increased linearly with temperature up to 300 K for concentrated samples. The linear dependence of relaxation rate on temperature is characteristic of a direct process, but Bowman and Kevan pointed out that this dependence could also be described by an Orbach-Aminov process with energy gap less than 1 K [10]. The aim of the present work is to examine relaxation with decreased dopant concentration and to determine the dependence of relaxation processes on concentration and microwave frequency.

2. Experimental

2.1 Preparation of samples

Two concentrations of DPPH in polystyrene were prepared: 5% (140 mM) and 0.01% (340 μM) by weight. DPPH and polystyrene beads (average MW 35,000), both Sigma Aldrich, were dissolved separately in dried toluene (Acros Organics) and then combined in the appropriate ratios. This solution was poured onto a large glass plate to form a thin film

which was loosely covered with foil and allowed to dry. The sample was scraped and placed in 4 mm (X-band) and 1.6 mm (Q-band) outer diameter quartz EPR tubes. The samples were evacuated for at least 3 hours (pressure < 5 mTorr) to remove oxygen and then sealed. Due to the photosensitivity of DPPH, samples were covered to partially exclude light during most of the preparation. Even with storage in the dark at -20°C , signal intensity decreased with time. Most measurements were performed on samples that had been stored for less than a week.

2.2 EPR spectroscopy

Pulse measurements were carried out on a Bruker E580 spectrometer using Bruker ER4118X-MD5-W1 (X-band) and ER5107D2 (Q-band) dielectric resonators. The spectrometer was equipped with an Oxford CF935 cryostat for measurements in the range 20–295 K. T_1 measurements were recorded by 3-pulse inversion recovery, and T_m measurements were recorded by 2-pulse spin echo decay. To reduce resonator ringdown, the X-band resonator was overcoupled to $Q < 150$, and the Q-band resonator was fully overcoupled ($Q \sim 100$). Microwave powers were adjusted to give the maximum echo at each temperature, using either 40 or 80 ns π pulse lengths. Spin lattice relaxation rates did not depend on pulse lengths. Spin echo decay times for the high concentration sample were pulse-length dependent. The shot repetition time (SRT) was always significantly longer than T_1 . The magnetic field for the relaxation time measurements was set for resonance on the center of the central line of the spectrum, which was approximately the maximum intensity of the absorption spectrum.

For the 140 mM sample, variations in T_1 were observed that are attributed to nonuniformity in concentration through the sample. X-band measurements at 295 K for the high concentration sample were repeated at different sample positions by rotating the sample and changing the vertical position in the resonator. Eighteen measurements were recorded on five different days, giving an average T_1 value of $6.7 \pm 2.0 \mu\text{s}$ and a range of values from 3.5 to 10 μs . This broad range and deviation demonstrates sample heterogeneity, and hence the importance of sample positioning for reproducibility. The values in Fig. 2 for the temperature dependence of T_1 were collected at the same position, except for the need to reposition when transitioning from liquid helium to liquid nitrogen at about 80 K.

CW EPR was used to examine the half-field transition of the 140 mM sample at X-band. Spectra were collected around g values of 2.0036 and 4.0072 on a Bruker EMX with an ER4122-SHQ resonator at room temperature. Parameters for both measurements were: 150 G sweep width, 100 kHz modulation frequency, 1.0 G modulation amplitude, and 0.6 mW power. Only the instrument gain and number of scans were modified to obtain the most accurate comparison between the two lines.

2.3 Data analysis

The experimental inversion recovery curves were not single exponentials. To characterize the distributions, outputs from several analysis programs were compared. *Multifit*, which is based on Provencher's algorithms [11], compares the quality of fits to single, double, and triple exponentials and assigns a weighting to each component. *UPEN* analyzes data in terms of a distribution of relaxation times [12, 13]. The presence of distributions of relaxation times in the DPPH data were confirmed by the outputs from UPEN. Inversion recovery data for solid samples may include contributions from spectral diffusion, as well as T_1 [14], so for data sets that were fit better with two components, the shorter component was attributed to spectral diffusion and the longer component to T_1 . Conversely, spin echo decay curves fit well to single exponential functions. T_m values were determined using Multifit with a single exponential. At 140 mM, T_m is dominated by spin diffusion, causing enhanced

relaxation rates [14]. Therefore, analysis of T_m data focused on the 340 μM sample, which is sufficiently dilute to decrease contributions from spin diffusion.

The processes contributing to T_1 were modeled using a locally-written *Mathcad* program which fits the temperature dependence of $1/T_1$ as a sum of individual contributions [14]. Modeling of the 340 μM data was based on Eq. 1,

$$\frac{1}{T_1} = A_{\text{dir}}T + A_{\text{Ram}} \left[\left(\frac{T}{\theta_D} \right)^9 J_8 \left(\frac{\theta_D}{T} \right) \right] + A_{\text{loc}} \left[\frac{e^{\Delta_{\text{loc}}/T}}{(e^{\Delta_{\text{loc}}/T} - 1)^2} \right] \quad (1)$$

where contributions to T_1 relaxation include direct [15], Raman [15], and local mode vibrations [16]. In Eq. 1, A refers to the coefficient for a given contribution and T is temperature (Kelvin). The Debye temperature is given by θ_D , while J_8 is the transport integral (Eq. 2). The energy separation for the local mode process is represented by Δ_{loc} .

$$J_8 \left(\frac{\theta_D}{T} \right) = \int_0^{\frac{\theta_D}{T}} x^8 \frac{e^x}{(e^x - 1)^2} dx \quad (2)$$

The fits to experimental data for the 340 μM sample were accomplished through iterations of contributions from the various processes, to minimize the sum of the squares of the residuals (Fig. 2). Since there is no known low-lying excited state, an Orbach process was not included in the analysis for the low concentration samples.

3. Results

3.1 Analysis of T_1 for 340 μM DPPH in polystyrene

For 340 μM DPPH in polystyrene, the distributions of relaxation times as a function of temperature obtained with the uniform penalty method (UPEN) [12, 13] are shown in Fig. 3. At X-band, the inversion recovery data at most temperatures fit well to a single exponential function, and the analysis showed predominantly a single peak in the distributions. The single component fits were used for the analysis of temperature dependence (Fig. 2). At Q-band, the analysis of the inversion recovery curves indicated two components at all temperatures (Fig. 3). The characteristic time for the slower process as calculated with a two component fit (Multifit) was attributed to T_1 . The relaxation rates at X-band and Q-band are similar, which indicates that the dominant contributions are frequency independent. Fig. 2 shows the contributions from each of the processes to T_1 for 340 μM DPPH in polystyrene. The values of the coefficients in Eq. 1 that gave the best fits to the experimental data were: (X-band) $A_{\text{dir}} = 0.2$, $A_{\text{Ram}} = 6.0 \times 10^3$, and $A_{\text{loc}} = 2.1 \times 10^4$; (Q-band) $A_{\text{dir}} = 0.3$, $A_{\text{Ram}} = 2.60 \times 10^3$, and $A_{\text{loc}} = 1.9 \times 10^4$. Values $\theta_D = 110$ K and $\Delta_{\text{loc}} = 500$ K were the same at both frequencies. The Raman process dominates relaxation at low temperatures, along with a small direct process contribution. A local mode becomes significant at high temperatures. The set of processes are similar at the two frequencies, with slightly increased direct process contribution at Q-band.

3.2 Analysis of T_1 for 140 mM DPPH in polystyrene

As reported by others, T_1 for DPPH doped in solid matrices is strongly concentration dependent [5–8] and relaxation rates for the 140 mM sample are orders of magnitude faster than at lower concentrations (Fig. 2). The strong electron-electron interactions in the 140 mM sample are confirmed by the observation of a half-field transition (Fig. 4), from which

an average electron-electron distance of about 9 Å was calculated [17], which is similar to the 13 Å expected if this concentration were uniformly distributed [18]. At this high concentration, analysis of inversion recovery curves becomes difficult due to the wide distribution of T_1 values that is attributed to localized concentration variations in the sample. Analysis of the data with UPEN showed broad and poorly defined distributions. The values in Fig. 2 are the longer components obtained by fits with two exponentials. At 140 mM, the relaxation rates at X-band and Q-band are similar and vary approximately inversely with temperature as reported previously [5–9]. The contributions from the Raman and local mode process that dominated for the low concentration sample are very small relative to the experimental relaxation rates for the high concentration sample. The absence of significant frequency dependence of T_1 rules out contributions from thermally-activated processes [19]. These rates (Fig. 2) are still significantly slower than the temperature-independent value of 0.2 μ s reported for magnetically concentrated DPPH at 28 MHz [20].

4. Discussion

4.1 340 μ M DPPH in polystyrene

The model in Eq. 1 for the temperature dependence of T_1 for the 340 μ M sample fit the experimental data very well. The relaxation rates for DPPH at 100 K and 298 K are compared with those for other organic radicals in dilute glassy matrices in Table 1. The overall trend at both temperatures is toward shorter relaxation times for larger deviation of g values from 2.0023. The dominant contributions to relaxation are the Raman process at 100 K and the local mode at 298 K, which also are the primary contributions to relaxation for other organic radicals in sucrose octaacetate at these temperatures [21]. The similar trends in relaxation times at the two temperatures indicate that A_{loc} and A_{Ram} are correlated, which suggests that both processes modulate spin orbit coupling.

The temperature dependence of T_m for the 340 μ M sample is shown in Fig. 5. $1/T_m$ is faster at about 140 K than at higher and lower temperatures. A similar enhancement in spin echo dephasing has been reported for a spin-labeled polystyrene [22]. The enhancement with maximum impact at about 140 K was attributed to a wagging motion of the phenyl groups of the polystyrene, which is likely to also apply to the DPPH in polystyrene sample. The increase in relaxation rates above about 200 K is attributed to softening of the polystyrene matrix.

4.2 140 mM DPPH in polystyrene

Strong electron-electron interactions dominate relaxation processes at X-band and Q-band for 140 mM DPPH in polystyrene and make the relaxation much faster than at lower concentrations. The relaxation times at 77 K at X-band and Q-band are 3.9×10^{-5} and 2.7×10^{-5} s, respectively. These values are similar to the previously reported values at 77 K at X-band (read from plots) of 8×10^{-6} s [5] and 2.5×10^{-5} s [9] for 140 mM DPPH in polystyrene. For 44 mM BDPA (1,3-bisdiphenylene-2-phenylallyl) in sucrose octaacetate between 90 and 290 K at Q-band, $1/T_1$ was approximately linearly dependent on temperature, although at lower concentrations its relaxation was dominated by Raman and local mode processes [23]. This dependence of $1/T_1$ on T is similar for the high concentration samples of both DPPH and BDPA. It has been proposed that the dependence of $1/T_1$ on T for DPPH is due to the direct process [9] or to an Orbach process with energy less than 1 K [10]. Frequency dependence is predicted for the direct process [24], so the similarity in relaxation rates for the high concentration DPPH sample at X-band and Q-band (Fig. 2) is not consistent with assignment of a direct process.

5. Conclusions

Inversion recovery measurements of T_1 for 140 mM DPPH in polystyrene confirm the results obtained in prior studies using continuous wave power saturation that T_1 varies approximately linearly with $1/T$. The similarity in relaxation rates at X-band and Q-band suggests that the primary contribution to T_1 relaxation at this high concentration may not be the direct process. At lower concentrations (340 μM), the temperature dependence of $1/T_1$ is similar to that of other organic radicals in glassy solvents, and is dominated by the Raman process and a local mode. A local minimum in T_m at about 140 K is consistent with prior assignment of phenyl motion within the polystyrene matrix.

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References

- Kolaczowski SV, Cardin JT, Budil DE. *Appl Magn Reson*. 1999; 16:293–298.
- Jang ZH, Suh BJ, Corti M, Cattaneo L, Hajny D, Borsa F, Luban M. *Rev Sci Instrum*. 2008; 79:046101–046101/046103. [PubMed: 18447559]
- Smolyaninov IV, Antonova NA, Poddel'sky AI, Smolyaninova SA, Osipova VP, Berberova NT. *J Organomet Chem*. 2011; 696:2611–2620.
- Schacher GE. *Phys Rev*. 1964; 135:A185–A190.
- Goldsborough JP, Mandel M, Pake GE. *Phys Rev Lett*. 1960; 4:13–15.
- Swanenberg TJB, Poullis NJ, Drewes GWJ. *Physica*. 1963; 29:713–720.
- Hoehrl G, Wolf HC. *Z. Physik*. 1965; 183:341–351.
- Yoshida H, Hayashi K, Okamura S. *Arkiv Kemi*. 1964; 23:177–189.
- Turkevich J, Soria J, Che M. *J Chem Phys*. 1972; 56:1463–1466.
- Bowman, MK.; Kevan, L. *Time Domain Electron Spin Resonance*. Kevan, L.; Schwartz, RN., editors. John Wiley; New York: 1979. p. 68–105.
- Provencher SW. *J Chem Phys*. 1976; 64:2772–2777.
- Borgia GC, Brown RJS, Fantazzini P. *J Magn Res*. 2000; 147:273–285.
- Borgia GC, Brown RJS, Fantazzini P. *J Magn Res*. 1998; 132:65–77.
- Eaton SS, Eaton GR. *Biol Magn Reson*. 2000; 19:29–154.
- Murphy J. *Phys Rev*. 1966; 145:241–247.
- Castle JG Jr, Feldman DW. *J Appl Phys*. 1965; 36:124–128.
- Eaton SS, More KM, Sawant BM, Eaton GR. *J Am Chem Soc*. 1983; 105:6560–6567.
- Chandrasekar S. *Rev Modern Phys*. 1943; 15:1–87.
- Atsarkin VA, Demikov VV, Vasneva GA. *Phys Rev B*. 1997; 56:9448–9453.
- van Gerven, L.; Van Itterbeek, A.; De Laet, L. *Paramagnetic Resonance*. Low, W., editor. 1963. p. 905–918.
- Sato H, Kathirvelu V, Fielding AJ, Bottle SE, Blinco JP, Micallef AS, Eaton SS, Eaton GR. *Mol Phys*. 2007; 105:2137–2151.
- Brown IM. *J Chem Phys*. 1976; 65:630–638.
- Sato H, Kathirvelu V, Spagnol G, Rajca S, Eaton SS, Eaton GR. *J Phys Chem B*. 2008; 112:2818–2828. [PubMed: 18284225]
- Davids DA, Wagner EP. *Phys Rev Lett*. 1964; 12:141–142.
- Sato H, Bottle SE, Blinco JP, Micallef AS, Eaton GR, Eaton SS. *J Magn Reson*. 2008; 191:66–77. [PubMed: 18166493]

Fig. 1.
Molecular formula for DPPH.

Fig. 2.

X-band (left) and Q-band (right) log-log plots of $1/T_1$ vs. temperature for 340 μM ($\diamond$) and 140 mM ($\circ$) DPPH in polystyrene. The contributions to T_1 (fit in solid black) for the 340 μM sample are the Raman process (large dash), a local mode (dot dash), and the direct process (small dash). The magnitude of each contribution is similar for the two frequencies.

Fig. 3.
X-band (left) and Q-band (right) UPEN analyses for 340 μM DPPH in polystyrene.
Different temperature ranges were used for clarity.

Fig. 4. Half field spectrum (left) and $g = 2.003$ spectrum (right) of 140 mM DPPH in polystyrene. Both spectra were recorded with 0.6 mW power and 1.0 G modulation amplitude at 100 kHz. The half-field transition is the average of 1280 scans, and the $g = 2.003$ signal was recorded in a single scan.

Fig. 5. X-band ($\blacktriangle$) and Q-band ($\bullet$) log-log plots of $1/T_m$ vs. temperature for 340 μM DPPH in polystyrene.

Table 1

T_1 values for organic radicals in glassy matrices at X-band.

Radical	Matrix	Conc. (mM)	g_{iso}	T_1 at 100 K	T_1 at ~298K	Reference
BDPA ^a	Sucrose octaacetate	< 3	2.0026	10 ms	1 ms	[21]
BDPA ^a	Polystyrene	0.2	2.0026	47 ms ^c	90 μ s	Unpublished results
DPPH	Sucrose octaacetate	< 3	2.0036	1 ms	100 μ s	[21]
DPPH	Polystyrene	0.34	2.0036	1.2 ms	65 μ s	This work
Galvinoxyl	Sucrose octaacetate	< 3	2.0044	300 μ s	8 μ s	[21]
TPHIO ^b	Sucrose octaacetate	< 3	2.0059	300 μ s	40 μ s	[21]
Tempone	1:1 water-glycerol	1	2.0059	150 μ s	N/A	[25]
Tempone	Sucrose octaacetate	< 3	2.0060	80 μ s	4 μ s	[21]

^a 1,3-bis(diphenylene-2-phenylallyl)

^b 1,1,3,3-tetraphenylisindolin-2-ylloxy

^c T_1 at 80 K