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Impact of molecular size on electron spin relaxation rates of nitroxyl radicals in glassy solvents between 100 and 300 K

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Abstract

Electron spin lattice relaxation rates were measured for 12 nitroxyls with molecular weights between 144 and 438, and for galvinoxyl, 1,3-bisdiphenylene-2-phenylallyl (BDPA), and 2,2-diphenyl-1-picrylhydrazyl (DPPH) in glassy sucrose octaacetate. Relaxation rates for polar nitroxyls also were measured in glassy sorbitol. Dependence on $V_{eff}^{-\gamma} T$ where V_{eff} is effective molecular volume and γ is a material-specific parameter, was used to compare processes. Values of V_{eff} were determined based on molecular libration in glassy sucrose octaacetate ($\gamma = 3.5$), tumbling in viscous decalin at 233 K ($\gamma = 4.7$), or tumbling in heavy mineral oil ($\gamma = 6.0$). For nitroxyl relaxation there is a master curve: $\log(1/T_1)$ vs $\log(V_{eff}^{-\gamma} T)$ ($\gamma = 0.89$). The similarity of the values of γ for the Raman process and for the additional process that contributes at higher temperatures, and the absence of frequency dependence between X- and Q-band, support assignment of this additional process as a local mode. For these radicals the contributions from the local mode and the Raman process are correlated and follow trends in spin-orbit coupling. The temperature dependence of spin echo dephasing in sucrose octaacetate is dominated by rotation of methyl groups and by a motional process analogous to the Raman process.

Keywords: nitroxyl radicals, spin-lattice relaxation, Raman process, local mode, volume scaling of thermodynamic parameters

1. Introduction

The majority of studies of spin-lattice relaxation rates, $1/T_1$, for organic radicals have focused on fluid solutions where modulation of anisotropic interactions by molecular tumbling dominates [1-5]. Less information is available on factors that influence relaxation rates in the slower motional regime that is characteristic of glassy solvents [6-8].

Deleted: tumbling

The processes that dominate T_1 for magnetically dilute samples change with temperature. At low temperature the single-phonon direct process dominates and $1/T_1$ is linearly dependent on temperature. In this process Zeeman energy is transferred to the lattice via a vibration with energy equal to the Zeeman energy. As temperature is increased the Raman process becomes increasingly important. This is a two-photon process in which the energy transferred to the lattice is the difference between the energies absorbed and emitted for a virtual excited state at any energy less than the Debye temperature [9]. The temperature dependence of the Raman process is given by equation (1).

$$\frac{1}{T_1^{Raman}} = C_{Ram} \left(\frac{T}{\theta_D}\right)^9 J_8\left(\frac{\theta_D}{T}\right) \quad (1)$$

where θ_D is the Debye temperature and J_8 is the transport integral,

$J_8\left(\frac{\theta_D}{T}\right) = \int_0^{\theta_D/T} x^8 \frac{e^x}{(e^x - 1)^2} dx$. The limiting behavior for the Raman process above the

Debye temperature results in relaxation that is proportional to T^2 (equation (2)).

$$\frac{1}{T_1^{Raman}} = C_{Ram}'' T^2 \quad (2)$$

Although the concept of the Raman process was developed for an ionic lattice, its characteristic temperature dependence has been observed for many systems including organic radicals in glassy solvents [4]. A previous study demonstrated that the Raman process for nitroxyl radicals is strongly solvent dependent [7]. One purpose of this work is to define characteristics of organic radicals that determine the value of C_{Ram}'' .

At higher temperatures, but below the glass transition temperature, $1/T_1$ for many paramagnetic centers changes more rapidly than T^2 , which indicates that one or more additional processes makes a significant contribution [4,6,7]. The second purpose of this work is to characterize this additional process for nitroxyl radicals. Possible candidates are a thermally-activated process [10,11], a local mode [12,13], or a β process [14-16].

The contribution to spin-lattice relaxation from a thermally activated process, for which the rate follows the Arrhenius equation, is described by equation (3) [10,11].

$$\frac{1}{T_1^{therm}} = C_{therm} \frac{\tau_{therm}}{1 + \omega^2 \tau_{therm}^2} \quad (3)$$

where ω is the electron spin Zeeman frequency, τ_{therm} is the correlation time for the dynamic process $= \tau_c^0 \exp(E_a/RT)$, E_a is the activation energy, and τ_c^0 is the pre-exponential factor. The contribution to the relaxation rate from this process depends on the Zeeman frequency. A local vibration mode [12,13] is also a two-phonon process, but unlike the Raman process it involves a single vibrational frequency that is above the Debye temperature. The temperature dependence of the contribution to the relaxation from a local mode is given by equation (4).

$$\frac{1}{T_1^{local}} = C_{local} \frac{Exp[\Delta_{loc} / T]}{(Exp[\Delta_{loc} / T] - 1)^2} \quad (4)$$

where C_{local} is the coefficient for the contribution from a local vibrational mode, and Δ_{loc} is the energy for the local mode, in Kelvin. This process is independent of Zeeman frequency. In studies of dielectric relaxation, β processes are invoked for the glassy state [14-16]. These processes are inherent properties of super-cooled liquids involving multiple modes of motion of the molecule as a whole and result in relaxation rates that are frequency dependent.

To separate the effects of molecular structure on spin-lattice relaxation from the impact of changes in spin-orbit coupling, it is helpful to keep g value constant. Since nitroxyl radicals with a range of structures have similar g values (and by implication similar spin-orbit coupling) a series of nitroxyl radicals with molecular weight ranging from 144 to 438 and differing structures (Figure 1) were studied. Several other organic radicals with different g values were included in the study for comparison of the effects of spin-orbit coupling.

Recent studies of thermodynamic properties of glass-forming liquids have demonstrated the utility of analyzing data in terms of the scaled parameter $T' = TV^\gamma$, where T' is the scaled temperature, V is molecular volume, γ is a material-dependent adjustable parameter, and T is temperature (K) [17-22]. If the intermolecular interactions that impact a physical observable are dominated by the Leonard-Jones repulsive term then the potential function is proportional to $V^{-\gamma}$ with $\gamma = 4$ [21]. For dielectric relaxation times it was proposed that the exponent γ provided a method to separate the effects of temperature and volume on the intermolecular interactions [18]. For a particular liquid, similar values of γ have been found in studies of dielectric relaxation, glass transition temperature, light

scattering, anharmonicity of lattice vibrations, and viscosity [18,21]. Values of γ range from 2.3 for polyglycol to 8 for the van der Waals liquid octane [20]. In this study the dependence of electron spin relaxation on molecular volume is examined as a possible means to distinguish between proposed relaxation processes.

(insert Figure 1 here)

2. Methods

2.1 Samples

2.1.1 Syntheses

(insert scheme 1 here)

Synthesis of 2-benzyl-1,1,3,3-tetraphenylisoindoline. A solution of N-benzylphthalimide (5 g, 0.021 mol) in dry toluene (50 mL) was added to a stirring ethereal solution of phenylmagnesium bromide made from dry Mg turnings (5.32 g, 0.22 mol) and bromobenzene (26 g, 0.17 mol) in dry EtO₂ (ca. 50 cm³). The EtO₂ was removed via Dean-Stark apparatus and the remaining mixture refluxed for 4 hours. The reaction mixture was allowed to cool to room temperature and any remaining phenylmagnesium bromide was quenched by the careful addition of 30% NH₄Cl (50 cm³) with constant stirring. This was followed by water (50 cm³) and NaHCO₃ (30 cm³). The layers were separated and the aqueous layer was thoroughly extracted with hexane (3 x 50 cm³). The organic layers were concentrated and subjected to basic alumina (activity I) column chromatography (initially 100% hexane to remove biphenyl by-product and then 95:5 hexane/ethyl acetate) The eluent was evaporated to give 2-benzyl-1,1,3,3-tetraphenylisoindoline as a white crystalline solid. (1.40 g, 13 %); δ_{H} (400.162 MHz, CDCl₃) 4.14 (2H, s), 6.27 (2H, dd), 6.83 (2H, dd) 6.90 (1H, dd), 7.12 - 7.14 (24H, m); δ_{C} (75.430 MHz, CDCl₃) 49.0 (C1, C3), 82.1 (CH₂), 125.2 (ArC), 126.5 (ArC), 127.0 (ArC), 127.67 (ArC), 127.72 (ArC), 129.6 (ArC), 130.5 (ArC), 141.2 (ArC), 145.6 (ArC), 146.1 (ArC).

Synthesis of 1,1,3,3-tetraphenylisoindolin-2-yloxy (TPHIO). 2-benzyl-1,1,3,3-tetraphenylisoindoline (500 mg, 0.97 mmol) was dissolved in 50 mL of dichloromethane. To this solution 50% *m*-chloroperbenzoic acid (1.35 g, 3.9 mmol) was added with stirring at room temperature under a normal atmosphere. The solution was then stirred for 6 days, replacing any dichloromethane lost to evaporation. After 6 days the reaction mixture was washed with 50 mL of saturated sodium bicarbonate solution, followed by 25 mL of brine,

and dried over sodium sulfate and the solvent evaporated to produce an orange oil. Purification by flash column chromatography (10:1 hexane/ethyl acetate) afforded 230.5 mg of 1,1,3,3-tetraphenylisoindolin-2-yloxyl as a brilliant orange crystalline solid (54 % yield 87% yield allowing for recovered starting material). (M.P. 250-251 °C *dec*)(lit 250-253 °C); NMR gave a broad amorphous spectrum, m/z (EI) 438.1859 (M^+ C₂₃H₂₅N requires 438.1858), 408 (52), 346 (60), 330 (100%), 253 (55), 165 (28).

1,1,3,3-Tetramethylisoindolin-2-yloxyl (TMIO) was prepared by the method of Griffiths et al. [23].

1,1,3,3-Tetraethylisoindolin-2-yloxyl (TEIO) was synthesised according to a modification of the synthesis of TMIO reported by Griffiths et al. [23]. The 2-benzyl-1,1,3,3-tetraethylisoindoline precursor decomposes above 250°C **before melting**, consistent with the literature [24]. The properties of the TEIO agreed with those reported previously [25].

2.1.2 Sample Preparation

2,2,6,6-tetramethyl-piperidine-1-oxyl (tempo), 4-hydroxy-2,2,6,6-tetramethylpiperidinoxyl (tempol), 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (tempone), 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-oxyl (CPROXYL), 3-carbamoyl-2,2,5,5-tetramethylpyrroline-1-oxyl (CTPO) (Aldrich Chemical Co. Milwaukee, WI), di-tert-butylnitroxyl (DTBN) (Eastman Kodak Co.), tempone-d₁₆, ¹⁵N-CTPO-d₁₃ (CDN Isotope) were used as received. 2,5-di-tert-butyl-3,4-bis(methoxycarbonyl)-1H-pyrrole-1-oxyl (tBuPyrr) was provided by Professor Andre Rassat. In addition to the nitroxyl radicals, 1,3-bisdiphenylene-2-phenylallyl (BDPA) and 2,2-diphenyl-1-picrylhydrazyl (DPPH), galvinoxyl (Aldrich Chemical Co. Milwaukee, WI) were studied. Sucrose octaacetate and sorbitol were Aldrich analytical grade and glycerol was Aldrich anhydrous grade. Decalin (a mixture of isomers) was purchased from City Chemical Corporation or Fisher Chemical. Heavy mineral oil (Sargent Welch, SC 13645), were specified to have viscosity of 300-320 SUS at 100 °F. Samples in sucrose octaacetate ($T_g = 298$ K) [26] or sorbitol ($T_g = 268$) [15] were prepared by grinding weighed portions of radical and host. The solid mixtures were placed in EPR tubes, evacuated to remove oxygen, heated above the melting point, and cooled. Samples were stored at 4°C or ambient temperature. The concentrations of solutes were less than 3 mM. In this concentration range relaxation rates for nitroxyl radicals in glasses are concentration independent.

2.2. EPR Spectroscopy

Continuous wave (CW) spectra were recorded on a Varian E9 or in the CW mode of an X-band saturation recovery (SR) spectrometer [27] using a TE₁₀₂ rectangular resonator. Fluid and rigid lattice spectra were simulated using locally-written software that included hyperfine couplings calculated by perturbation theory to second order [28]. It was assumed that the axes of the g and A matrices are coincident. g -Values were calibrated relative to solid DPPH (diphenylpicryl-hydrazyl, $g = 2.0036$) or polycrystalline BDPA (bisdiphenylallyl, $g = 2.0026$). Values of g_{zz} and A_{zz} are readily determined. At X-band the values of A_{xx} , A_{yy} , g_{xx} , and g_{yy} are harder to evaluate. Values of these parameters were constrained by requiring that the average g and A values from the rigid lattice spectra agree with the isotropic g and A values measured in fluid solution in the same solvent. The primary use of the g and A values was in the calculation of the tumbling correlation times. The calculated values of the tumbling correlation times are more sensitive to the anisotropies between parallel (g_z or A_z) and perpendicular values (average of g_x and g_y or A_x and A_y) than to the much smaller anisotropies within the perpendicular plane.

Most of the SR curves were recorded on the X-band spectrometer [27]. The Q of the resonator was ~ 3000 and the deadtime following a pulse for SR was $\sim 1.5 \mu\text{s}$. A Varian flowthrough dewar and temperature controller and nitrogen gas cooled with liquid nitrogen were used for temperatures above 100 K. To continuously monitor sample temperatures a thermocouple was positioned in the resonator, slightly above the active volume. To more precisely measure the temperature of the sample, immediately after each SR measurement the sample tube was replaced with a 4 mm i.d. quartz tube containing a thermocouple immersed in 3-methylpentane or glycerol. Some of the SR and inversion recovery curves and the two-pulse spin-echo decays at X-band and Q-band were recorded on a Bruker E580 with a SuperQFT bridge and loop-gap resonators, and an Oxford ESR935 cryostat with cernox sensor adjacent to the resonator.

SR, inversion recovery, and spin echo decays were recorded at the position of maximum intensity in the absorption spectrum. To investigate the orientation dependence, SR curves also were recorded at the g_{zz} position of the nitroxyl spectra. Values of T_1 were obtained by fitting a single exponential to the experimental curves. The temperature dependence of $1/T_1$ was modeled by fitting to the sum of contributions from the high-temperature limit of the Raman process (equation (2)) and an additional process that may be thermally-activated (equation (3)) or a local mode (equation (4)). Modeling the temperature dependence of $1/T_1$ in the high temperature limit of the Raman process requires a single adjustable parameter C_{Ram}'' which is well defined by the experimental data.

For the local mode and thermally-activated process there are two or three, respectively, adjustable parameters and the values of those parameters are correlated. Therefore, comparisons of the contributions from the additional relaxation process that contributes at higher temperature were based on magnitudes relative to the Raman process rather than on simulation parameters.

Values of T_m , the spin echo dephasing time constant, were calculated by fitting a single exponential to the decays ($Y(\tau) = Y(0)\exp(-2\tau/T_m)$). Although fits to some data sets could be improved by using a stretched exponential, it is useful to monitor a single parameter when displaying trends with temperature. For samples with echo envelope modulation, the mid-points of the modulation were used for the fitting.

2.3. Libration

The temperature dependence of nitroxyl A_{zz} in glassy solvents is attributed to librational motion that averages components of the anisotropic nitrogen hyperfine splittings [29,30]. Since A_{xx} and A_{yy} are smaller than A_{zz} , changes in A_{zz} with temperature can be assigned to motions that average A_{zz} with either A_{xx} or A_{yy} . The corresponding increases in A_{xx} or A_{yy} are difficult to monitor because these splittings are not well resolved. If the motion is restricted to oscillations in a plane and occurs around the nitroxyl x -axis, which is defined as the N-O bond [31,32], motion averages the y and z components of the hyperfine splitting.

$$A'_{xx} = A_{xx} \quad (5)$$

$$A'_{yy} = A_{yy} + (A_{zz}-A_{yy})\langle\sin\alpha^2\rangle \quad (6)$$

$$A'_{zz} = A_{zz} - (A_{zz}-A_{yy})\langle\sin\alpha^2\rangle \quad (7)$$

where α is the angular deviation from equilibrium and $\langle\alpha\rangle = 0$. For small amplitudes of motion one may replace $\langle\sin\alpha^2\rangle$ by $\langle\alpha^2\rangle$ [29,30,33]. To accurately define values of A'_{zz} , second-derivative displays of the EPR spectra were used. The slopes of plots of A'_{zz} vs. temperature were approximately independent of temperature, which indicates that the mean-squared amplitude of librational motion, $\langle\alpha^2\rangle$, is proportional to temperature and can be modeled as in equation (8) [33].

$$\langle\alpha^2\rangle = a_{\text{libration}} T \quad (8)$$

The slope is approximately independent of temperature if the frequency of the librational mode is constant, and the energy of the system increases proportional to temperature. This behavior is typical of harmonic solids.

Substitution of (8) into (7) gives

$$A'_{zz} = A_{zz} - (A_{zz} - A_{yy}) (a_{\text{libration}} T) \quad (9)$$

$$\text{Therefore, } (\Delta A'_{zz} / \Delta T) = -a_{\text{libration}} (A_{zz} - A_{yy}) \quad (10)$$

where $\Delta A'_{zz} = A'_{zz} - A_{zz}$. Since there is little variation in $A_{zz} - A_{yy}$ within the series of nitroxyl radicals studied, $(\Delta A'_{zz} / \Delta T)$ can be used as a measure of $\langle \alpha^2 \rangle$.

2.4. Tumbling in viscous solution

Nitroxyl tumbling correlation times were calculated from spectra of solutions in heavy mineral oil or in decalin using the NLSL program [31,34]. The solvents and temperatures for these experiments were selected such that the tumbling correlation times for the largest and smallest nitroxyls fell within the range for which τ values could be estimated. Nitroxyls with approximately isotropic tumbling were selected for this portion of the study and the spectra were analyzed in terms of the parallel (R_{\parallel}) and perpendicular (R_{\perp}) components of the rotational diffusion rate constant [34]. The g - and A -values were obtained from the rigid lattice and rapid-tumbling spectra. The g values that were used in the calculations of the tumbling correlation times were $g_{xx} = 2.0094$, $g_{yy} = 2.0060$, and $g_{zz} = 2.0024$. Because of libration, values of A_{zz} are temperature dependent, so extrapolation to $T = 0$ K was used to estimate the values of A_{zz} that were used in the calculations of the tumbling correlation times. The values of A_{zz} , A_{yy} , and A_{xx} (in gauss) were: DTBN (4.4, 4.4, 36.5); tempo (4.9, 4.9, 36.2); tempone (3.7, 3.7, 35.1); TMIO (3.4, 3.4, 34.5); TEIO (3.2, 3.2, 33.8); TPHIO (3.2, 3.2, 31.8). The x axis and z axis are along the direction of the N-O and along the π orbital of nitrogen [32], respectively, and these were defined as the axis for R_{\perp} . The y axis is perpendicular to the direction of NO bond and the π orbital of nitrogen, and this was defined as the axis for R_{\parallel} . The tumbling correlation times were calculated as $\tau = 1 / (6 \sqrt[3]{R_{\parallel} R_{\perp}^2})$.

3 Results and Discussion

3.1. Spin lattice relaxation, $1/T_1$, for nitroxyl radicals

3.1.1. Temperature Dependence. Representative plots of $\log(1/T_1)$ vs. $\log(T)$ in sucrose octaacetate or sorbitol between 100 and 300 K are shown in Figure 2. In sucrose octaacetate the relaxation rates increase in the order TPHIO < TEIO < CTPO < tempone < DTBN which is the order of decreasing molecular weights. In the hydrogen-bonded sorbitol glass, relaxation rates are slower than in sucrose octaacetate and increase in the order CTPO < tempol < tempone < DTBN, which again is the order of decreasing molecular weights.

Temperatures above 100 K are high enough that the Raman process for the nitroxyl radicals is described by equation (2) and relaxation rates are proportional to T^2 . The dotted lines in Figure 2 are the fits that would be obtained if the Raman process were the only contribution. The coefficients for the Raman process, C_{Ram}'' , decrease as molecular weight increases (Table 1). For this range of organic molecules, densities are expected to be similar, so molecular volumes are likely to be approximately proportional to molecular weights. This assumption was confirmed by calculation of the Connolly solvent-excluded volumes using the program Chem3D (CambridgeSoft, Cambridge, MA) (Table 1). The trends in C_{Ram}'' suggest a correlation with molecular volume.

(insert Table 1 here)

For TPHIO the temperature dependence predicted for the Raman process fits the experimental data reasonably well over most of the range examined. However, for the other radicals there is substantial deviation between the observed temperature dependence of $1/T_1$ and the T^2 dependence for the Raman process, which indicates that one or more additional processes make significant contributions. The solid fit lines in Figure 2 were calculated as the sum of contributions from the Raman process and a thermally-activated process. Over this limited temperature range the fit lines obtained with a local mode as the second process were indistinguishable from the lines shown in the plot.

(insert Figure 2 here)

3.1.2. Comparison of the dependence of the Raman coefficients, libration, and tumbling correlation times on molecular volume. Molecular tumbling in a viscous solution or libration of a molecule in a glassy matrix requires motion of the molecule as a

whole relative to surrounding solvent molecules and therefore reflects the dependence of motion on intermolecular interactions. The temperature dependence of A_{zz} for DTBN (Figure 3), tempo, tempone, CTPO, TMIO, TEIO, and TPHIO in sucrose octaacetate and for DTBN, tempone, and CTPO in sorbitol was measured to determine the impact of molecular size and solvent on libration (Table 2). Libration decreases dramatically as the size of the molecule increases. When a smaller range of molecular sizes was examined previously, the impact of nitroxyl size on libration was not evident [29,35]. The libration of nitroxyls in low polarity sucrose octaacetate is about 2.5 times larger than in hydrogen-bonded sorbitol, which is consistent with literature reports that stronger intermolecular interactions in the solvent decrease solute libration [29].

(insert Figure 3 here)

The tumbling correlation times for DTBN, tempo, tempone, TMIO, TEIO, and TPHIO were measured in decalin and in heavy mineral oil. The measurements in decalin were performed at 233 K to slow motion sufficiently that τ was in a range that could be determined from the intermediate tumbling spectra (Figure 4). The largest solute, TPHIO, tumbles most slowly, and has τ values that are 107 and 46 times longer than for tempone in mineral oil or decalin, respectively.

(insert Figure 4 here)

Parameters for tumbling and libration were plotted as a function of the Raman coefficient (Figure 5). To have all variables in units of seconds, τ , $(1/C_{Ram}^n)^{-0.5}$, and $1/\langle \alpha^2 \rangle$ are used. The choice of square root of the Raman coefficient is based on the fact that the Raman coefficient multiplies T^2 , whereas libration or tumbling vary linearly with temperature. Experimental values were normalized to 1 for tempone. On this log-log plot the slopes reflect differences in the exponent for the dependence on molecular size. The slopes greater than 1 for libration and molecular tumbling indicate that these processes are more strongly dependent on molecular size and intermolecular interactions than C_{Ram}^n . The slope of a plot of C_{Ram}^n in sorbitol vs C_{Ram}^n in sucrose octaacetate (not shown) is about 1, which indicates that although the coefficients are smaller in sorbitol than in sucrose octaacetate, the dependence on molecular size is similar.

(insert Figure 5 here)

3.1.3 Estimation of effective volumes. The values in Table 2 and the correlations in Figure 5 indicate a dependence of tumbling, Raman coefficients, and librational amplitude on molecular weight. Literature reports of the use of V^l as a scaling parameter for

interpretation of thermodynamic parameters that depend on intermolecular forces [18,19] suggest that it might be useful to formulate the comparisons in terms of molecular volumes. The slopes of the lines in Figure 5 suggest substantial differences in γ that could help to separate the effects of differing motions on electron spin relaxation rates. If the assumption is made that densities are similar and data are plotted as a function of molecular volume (not shown), there is scatter in the plots. The scatter suggests that it would be useful to define effective molecular volumes for the molecules. Although effective volume is expected to approximately correlate with molecular weight, discrepancies may arise because of variations in densities or deviations from spherical shapes.

NLSL simulations [31,34] of the intermediate tumbling spectra for DTBN, tempo, tempone, TMIO, TEIO, and TPHIO indicate that tumbling is close to isotropic so the effective volumes and actual volumes are expected to be similar for these molecules. This set of molecules was selected for calculation of the material-dependent exponent, γ . For each nitroxyl the effective volume, V_{eff} , relative to the volume of tempone, V_{tempone} , was estimated as $(V_{\text{eff}}/V_{\text{tempone}})^\gamma = \tau/\tau_{\text{tempone}}$ for the tumbling correlation time and $(V_{\text{eff}}/V_{\text{tempone}})^\gamma = \alpha_{\text{libration_tempone}}/\alpha_{\text{libration}}$ for libration, respectively. To take account of the T^2 dependence of the Raman process it was assumed that $(V_{\text{eff}}/V_{\text{tempone}})^\gamma = (C_{\text{Ram}}^n/C_{\text{Ram_tempone}}^n)^{-0.5}$. For each type of measurement the value of γ was determined by minimization of $\sum((V - V_{\text{eff}})/V)^2$ where $V = Mw/\text{density}$, which assumes that the densities of the molecules are same. The values of γ were then used to calculate the corresponding values of V_{eff} for this set of approximately spherical radicals (Table 3). The overall pattern is that the effective volumes calculated from tumbling, libration, and the Raman process are similar (Table 3), which indicates the plausibility of attributing the variations in the three physical observables to changes in molecular volume. For the other nitroxyls studied, the values of C_{Ram}^n and $\gamma = 0.89$ were used to calculate $V_{\text{eff}}/V_{\text{tempone}}$ (Table 1). For the larger set of nitroxyls there is again an approximate correlation of V_{eff} with molecular weight. The small values of V_{eff} relative to molecular weight for tBupyrr and for doxyl cyc in Table 1 suggest that the large carboxy methyl or long aliphatic side chains, respectively, play a rather small role in the spin-lattice relaxation because motions of those groups are not tightly coupled to motions in the regions of larger spin densities.

(insert Table 3 here)

3.1.4 Spin-lattice relaxation rates scaled by $V^{-\gamma}T$. The spin-lattice relaxation rates for the series of nitroxyls plotted as a function of $\log(V^{-\gamma}T)$ (Figure 6) fall along a single master curve. In sucrose octaacetate (Figure 6a) the congruence of the curves extends over the full temperature range that encompasses the regimes in which the Raman process and the higher temperature additional process make significant contributions. This observation indicates that the volume dependence and values of γ are similar for the two processes. In sorbitol (Figure 6b) the congruence is excellent in the temperature range for the Raman process, but there is more scatter at higher temperature where the additional process makes a larger contribution.

(insert Figure 6 here).

3.1.5 Characterization of the additional relaxation process. The contribution from the Raman process that had been identified by simulation (Figure 2), was subtracted from $1/T_1$ to calculate the contribution from the additional process $1/T_1^{\text{ADD}}$ at higher temperatures (Equation (11), Figure 7).

$$\frac{1}{T_1^{\text{ADD}}} = \frac{1}{T_1} - \frac{1}{T_1^{\text{Raman}}} \quad (11)$$

The values of $1/T_1^{\text{ADD}}$ show much greater dependence on molecular size in sucrose octaacetate than in sorbitol (Figure 7a). To make the curves for $1/T_1^{\text{ADD}}$ for the several nitroxyls overlap with the curve for tempone in sucrose octaacetate required $\gamma = 0.89$, which is similar to the scaling parameter for the Raman process. However, to make the curves for the several nitroxyls in sorbitol overlap with the curve for tempone required $\gamma \sim 0.35$. Although this value of γ has greater uncertainty because of the small number of comparison data sets, it is evident that solvent impacts γ . The values of γ for the Raman and additional process are much smaller than for molecular tumbling or libration, which indicates that molecular reorientation does not dominate the Raman or additional process. In NMR and dielectric relaxation studies, β processes are proposed for this temperature regime. However, the pressure-dependence of β processes and the relationship between β processes and glass transition temperatures indicate values of γ that are similar to those for tumbling ($\gamma = 4$ to 6), which is denoted as the α process [15,36]. The much smaller value of γ for the additional process (0.89) is not consistent with assignment as a β process. The similarity of the γ value for the additional process to that for the Raman process suggests that the additional process in sucrose octaacetate also is an intramolecular process, such as a local mode that involves many atoms of the molecule. In sorbitol the much smaller value of γ and the much weaker dependence of $1/T_1^{\text{ADD}}$ on molecular size

indicates that the nature of the mode has changed. Since sorbitol is a hydrogen-bonded solvent, there is the possibility of hydrogen bonding to the nitroxyl NO group and coupling of motions of the nitroxyl to motions of the solvent lattice.

(insert Figure 7 here)

3.1.6 Comparison of molecule-dependent scaling parameters. Prior studies examined the scaling effects of V' for pure liquids. When, for example, pressure was increased, volume became smaller and intermolecular interactions increased because molecules were forced closer together. In those experiments the exponents were positive because smaller molecular volumes corresponded to increased interactions. When properties, such as viscosity, are analyzed for molecules with different sizes, the surface area increases with molecular size, so solute-solvent interactions are increased, which is the opposite of the pressure effects on intermolecular interactions and the scaled expression has a negative exponent, $V_{\text{eff}}^{-\gamma}T$. The EPR experiments provide the opportunity to examine the properties of a solute molecule. The values of $\gamma=4.7$ and 6.0 for tumbling in low polarity decalin and sucrose octaacetate are similar to what was found for pure solvents, $\gamma=4$ for o-terphenyl, 4.8 for p-bis-(phenylethyl)benzene, and 7.5 for toluene [20]. For the local mode [contribution to spin-lattice relaxation](#) the much smaller value of $\gamma(0.35)$ in sorbitol than in low polarity sucrose octaacetate (0.89) is consistent with observations on other systems that γ is much smaller in hydrogen-bonded solvents than in non-polar solvents [20,21].

3.2 Comparison of $1/T_1$ for nitroxyls and other organic radicals

The temperature dependence of relaxation rates for nitroxyl radicals was compared with rates for magnetically dilute DPPH, galvinoxyl, and BDPA in sucrose octaacetate glasses (Figure 8). Near 100 K the Raman process dominates and the rates increase in the order BDPA < DPPH < TPHIO \sim galvinoxyl < tempone. The coefficients for the Raman process for these radicals are summarized in Table 4. As temperature increases, an additional process contributes to a greater extent for the faster relaxing tempone and galvinoxyl than for the slower relaxing radicals. There is little difference in relaxation rates between X-band and Q-band. The lack of frequency dependence is expected for the Raman process. The absence of frequency dependence for the additional process is consistent with assignment to a local mode and not to a thermally-activated process, such as methyl rotation [3].

(insert Figure 8 and Table 4 here).

The contributions to relaxation from the Raman process and from the additional process for BDPA, galvinoxyl, DPPH, and tempone in sucrose octaacetate and trityl

radical in 1:1 water glycerol (Figure 9) are correlated. Within the series of nitroxyl radicals all of the points on the plot of $\log(1/T_1^{\text{ADD}})$ vs. $\log(1/T_1^{\text{Raman}})$ fall on approximately the same line. That line is substantially offset from the lines for galvinoxyl or trityl (Figure 9a). The arrows in Figure 9a highlight the fact that addition of the same value to the x and y coordinates for points along the trityl or galvinoxyl curves can make those point coincide with points along the curve for tempone. Since addition of a constant on a log scale is equivalent to multiplication by a number that is greater than 1, the offsets between the curves suggest that choice of an appropriate scaling factor could make the data fall along one master curve. The scaled values are shown in Figure 9b and the corresponding scaling factors, C_{RA} , are summarized in Table 4.

(Insert Figure 9 here)

Deviations from $g_e = 2.00232$ are indications of the magnitude of spin-orbit coupling. Modulation of spin-orbit coupling by molecular motions contributes to spin-lattice relaxation, so increases in spin-orbit coupling are expected to cause increased relaxation rates [4]. Spin-lattice relaxation rates from the Raman process, $1/T_1^{\text{Raman}}$, are proportional to the square of spin-orbital coupling [37] so values of C_{Ram}'' and C_{RA} should be

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compared with $(g-g_e)^2$ [38] to examine the dependence on spin-orbit coupling (Table 4).

When comparing the different types of radicals, trends in C_{Ram}'' generally follow trends in $(g-g_e)^2$. However, comparisons of relaxation rates for different nitroxyl radicals indicate that even when g values are similar, there can be substantial differences in C_{Ram}'' that are

attributed to difference in size and structure of the radical. The correlation between the contributions to relaxation from the Raman and the local mode in low polarity solvents (Figure 9), indicates that molecular structure and solute-solvent interactions impact the two processes similarly. The offset between the curves in Figure 9a is then attributed to factors other than the volume-dependent motions of the radicals. Trends in C_{RA} (Table 4) parallel trends in $(g-g_e)^2$. We propose that C_{RA} provides a way to distinguish the effects on spin-lattice relaxation due to changes in spin-orbit coupling and spin delocalization from effects of molecular size and flexibility.

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3.3 Spin echo dephasing rates $1/T_m$ of nitroxyl radicals

It is also of interest to compare the motional processes that determine T_1 with ones that determine spin echo dephasing. The dephasing rate, $1/T_m$, in the glassy state reflects the impact of processes such as molecular motion and instantaneous diffusion that take

spins off resonance, as well as electron-electron spin-spin interaction. For organic radicals in proton-containing solvents, the dominant contributions to dephasing are proton spin diffusion [39,40] at low temperature and dynamic processes that modulate inequivalences at higher temperatures [4]. For tempone doped in a single crystal, the effects on T_m of methyl rotation, libration, and interconversion of twist-boat conformations were distinguishable [41].

3.3.1 Impact of methyl rotation. Rotation of a nitroxyl ring methyl group at a rate comparable to differences in electron-nuclear couplings that are averaged by the rotation enhances electron spin echo dephasing between about 100 and 200 K (Figure 10) [4,41,42]. This process is not observed for TPHIO, which contains no methyl groups. The temperature at which this effect is greatest depends on the barrier to rotation. The activation energy is lowest for the methyl group on the ethyls of TEIO and higher for the gem-dimethyls of tempone, TMIO, and CTPO (Figure 10). For the t-butyl groups of t-Bupyrr and galvinoxyl there are inequivalent methyls with two distinguishable barriers to rotation. The observation of enhanced echo dephasing for all of the radicals that contain methyl groups, but not for TPHIO, confirms prior studies that emphasize the importance of methyl groups in nitroxyl spin echo dephasing [4,8,41,43]. Unlike the trends in the spin-lattice relaxation, the barriers to rotation in these molecules are determined by local steric interactions and not by the size of the molecule. The significant differences in the activation energies for methyl rotation for the various nitroxyl radicals that is demonstrated in the spin echo dephasing predicts that if methyl rotation were a significant contribution to spin-lattice relaxation for these nitroxyls, the characteristic energy for the thermally-activated process should vary. The contributions from the additional spin-lattice relaxation process do not correlate with trends in the barriers to methyl rotation. This observation confirms the conclusion drawn from the lack of a frequency dependence that the additional spin-lattice relaxation process is not dominated by methyl rotation.

(insert Figure 10 here)

3.3.2 Impact of other motions on spin echo dephasing. As temperature increases, the impact of methyl rotation causes $1/T_m$ to go through a maximum. On the high temperature side of the maximum the rates do not return to the level observed at low temperature. Instead, there is a local minimum followed by further increase in $1/T_m$. The underlying trend toward faster $1/T_m$ with increasing temperature is attributed to motions that take spins off resonance on the timescale of the spin echo experiment. The contribution from these

motions is more readily seen for TPHIO because there is no contribution to $1/T_m$ from methyl rotation. The processes that contribute to this dephasing have been referred to as libration [35,44], but without invoking a specific motion as has been done for the temperature dependence of A_{zz} [30]. These observations raise the question how the motions that impact spin echo dephasing relate to the motions that contribute to spin-lattice relaxation. The temperature dependence of spin-echo dephasing rates for DTBN, tempone, CTPO, TMIO and TPHIO in sucrose octaacetate were replotted as a function of $V_{\text{eff}}^{-\gamma} T$ (Figure 11a,b) using γ calculated from the libration ($\gamma=3.5$) or Raman processes ($\gamma=0.89$) in the spin-lattice relaxation data. As expected, the maxima in $1/T_m$ resulting from methyl rotation still do not overlap on the rescaled plots because molecular volume is not the controlling parameter. Extrapolation of the dependence of $1/T_m$ for TPHIO for $\gamma=3.5$ predicts a faster increase with increasing $V_{\text{eff}}^{-\gamma} T$ than is observed for the other radicals (Figure 11a). By contrast the prediction for $\gamma=0.89$ appears to be consistent with the underlying temperature dependence for the methyl-containing radicals. The better agreement with $\gamma=0.89$ than with $\gamma=3.5$ suggests that the relevant motions in this temperature interval are many intramolecular vibrations, as in the Raman process, rather than a single dominant librational mode. These experiments were performed in a temperature regime below the glass transition temperature; a regime in which CW spectra are in the slow motion regime. In solvents with lower glass transition temperatures the onset of faster tumbling would lead to a larger value of γ , similar to that for tumbling. For radicals containing t-butyl groups the effects of methyl rotation extend to such high temperatures that it was not possible to characterize the impact of the underlying motional process.

4 Conclusions

Spin-lattice relaxation rates for nitroxyl radicals (MW = 144 to 439) in glassy solvents decrease as the molecular weight increases. The dependence on molecular size was parameterized with an effective volume and γ , which is a material-specific parameter that reflects the importance of intermolecular interactions. A master curve for spin-lattice relaxation for 12 nitroxyl radicals was obtained by plotting rates as a function of $V_{\text{eff}}^{-\gamma} T$ with $\gamma=0.89$. In low-polarity sucrose octaacetate the same values of γ were observed for the Raman process and for the additional process that contributes at higher temperatures. The additional process was independent of frequency between X- and Q-band. Differences in activation energies for methyl groups do not correlate with trends in spin-lattice relaxation rates. These three observations support assignment of the additional process as

a local mode rather than a thermally-activated process. The smaller value of γ (0.35) for the contribution from the local mode in the hydrogen bonding sorbitol glass suggests that hydrogen-bonding to the nitroxyl NO group couples motions in the radical to motions in the glassy solvent, which decreases the dependence on the size of the nitroxyl. The value of $\gamma = 0.89$ for the Raman processes in either sucrose octaacetate or sorbitol and for the local mode in sucrose octaacetate is much smaller than the $\gamma = 3.5$ observed for libration of nitroxyls in sucrose octaacetate or $\gamma = 4.7$ or 6 for tumbling in decalin or heavy mineral oil, respectively. The large difference in the values of γ emphasizes the distinction between the largely intramolecular vibrational modes that contribute to relaxation via the Raman process and reorientational motion (libration or tumbling) that is constrained by solute-solvent interactions. For nitroxyls, galvinoxyl, and trityl, the contributions to relaxation from the Raman and local mode processes are correlated – factors that increase one process also increase the other. Increasing deviations of g values from g_e contribute to faster relaxation by both processes. There is substantial similarity in the relaxation processes for a variety of radicals.

For radicals that contain methyl groups, rotation of the methyl groups at rates comparable to inequivalences in electron-proton couplings enhance spin-echo dephasing. The rates of methyl rotation are determined by local steric effects and do not depend upon the size of the molecule. Underlying the temperature dependence of $1/T_m$ that arises from the effects of methyl rotation is a gradual increase in $1/T_m$ with increasing temperature. The dependence of that process on molecular size varies approximately as $V_{\text{eff}}^{-\gamma}$, with $\gamma = 0.89$, which is similar to the size dependence of the Raman process and not that of libration or tumbling. This comparison suggests that the gradual enhancement of spin echo dephasing below the glass transition temperature arises from a range of vibrational modes and not from a single librational mode.

Acknowledgements.

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Table 1. Raman coefficients in sucrose octaacetate and sorbitol^a

Nitroxyls (Mw)	Sucrose octaacetate				sorbitol C_{Ram}''
	C_{Ram}''	$V_{eff}/V_{tempone}^b$	$V_{eff}/V_{tempone}^c$	$Mw/Mw_{tempone}$	
DTBN (144.2)	1.56	0.83	0.96	0.85	0.65
tempo (156.3)	1.0	1.07	1.0	0.92	
tempone (170.2)	1.20	1	1	1.00	0.47
amino-tempo (171.3)	0.84	1.17	1.04	1.01	
tempol (172.2)	0.89	1.14	1.03	1.01	0.37
CTPO (183.2)	0.78	1.22	0.99	1.08	0.31
tempone-d ₁₆ (186.2)	1.15	0.99		1.09	0.45
CProxyl (185.2)	0.73	1.27	1.04	1.09	
TMIO (190.3)	0.7	1.3	1.09	1.12	
¹⁵ N-CTPO-d ₁₃ (197.3)	0.54	1.5		1.15	0.23
TEIO (246.4)	0.53	1.52	1.51	1.45	
tBuPyrr (310.4)	0.79	1.22	1.73	1.82	
Doxyl cyc (342.4)	0.83	1.18	1.94	2.01	
TPHIO (438.5)	0.26	2.26	2.29	2.58	

^aUncertainties for C_{Ram}'' range from about $\pm 5\%$ for TPHIO for which there is a long temperature range in which the Raman process dominates to about $\pm 10\%$ for data sets with extensive overlap of the Raman and additional processes.

^bDetermined from tumbling and librational processes.

^cRatios of Connolly solvent-excluded volumes, calculated with Chem3D.

Table 2. Dependence of tumbling correlation times and libration on molecular size

Nitroxyl (Mw)	Tumbling time, τ (s)		$\Delta A_{zz}/\Delta T$ (G/K)	$\Delta A_{zz}/\Delta T$ (G/K)
	Decalin ^a	Mineral oil ^a	Sucrose octaacetate	Sorbitol
DTBN (144)	1.9×10^{-11}	2.2×10^{-11}	1.8×10^{-2}	7.3×10^{-3}
Tempo (156)	3.4×10^{-11}	4.1×10^{-11}	1.2×10^{-2}	
Tempone (170.2)	4.7×10^{-11}	5.1×10^{-11}	1.1×10^{-2}	4.2×10^{-3}
CTPO (183.2)			5.0×10^{-3}	1.9×10^{-3}
TMIO (190.3)	1.7×10^{-10}	3.6×10^{-10}	4.2×10^{-3}	
TEIO (246.4)	3.5×10^{-10}	5.4×10^{-10}	2.2×10^{-3}	
TPHIO (438)	2.2×10^{-09}	5.4×10^{-09}	5.9×10^{-4}	

^a Measurements were done at 233 K for decalin and 294 K for heavy mineral oil.

Table 3. Effective molecular volumes^a

Nitroxyl (Mw/Mw _{tempone})	Tumbling process		Libration process	Raman process ^b	Additional process ^c
	Decalin $\gamma = 4.7$	Mineral oil $\gamma = 6.0$	Sucrose octaacetate $\gamma = 3.5$	Sucrose octaacetate $\gamma = 0.89$	
DTBN (0.85)	0.83	0.87	0.86	0.83	0.82
tempo (0.92)	0.93	0.96	0.97	1.07	
tempone (1.0)	1	1	1	1	1
CTPO (1.08)			1.24	1.24	1.23
TMIO (1.12)	1.32	1.39	1.3	1.3	1.29
TEIO (1.45)	1.53	1.48	1.56	1.52	1.55
TPHIO (2.57)	2.27	2.17	2.28	2.26	2.28

^a $V_{\text{eff}}/V_{\text{tempone}}$ calculated from τ , $\langle \alpha^2 \rangle$, C_{Ram}'' and $(1/T_1^{\text{ADD}})$ for the set of approximately spherical nitroxyls that were used to determine values of γ .

^b In sucrose octaacetate or in sorbitol

^c In sucrose octaacetate

Table 4. Comparison of relaxation rates for organic radicals with different isotropic g-values

Radical	g-value	$(g-g_e)^2/(g_{\text{tempone}}-g_e)^2$ ^a	C_{RA}	C_{Ram}^*
Tempone	2.0060 ^b	1.0	1.0	1.2
TPHIO	2.0059 ^b	1.1 to 0.85	1.0	0.26
Galvinoxyl	2.0044 ^c	0.37 to 0.27	0.13	0.29
DPPH	2.0036 ^d	0.15 to 0.098	0.25	0.096
Trityl	2.0026 ^e	0.011 to 0.0023	0.022	0.074
BDPA	2.0026 ^f	0.011 to 0.0023	0.040	0.0095

^a The range corresponds to an uncertainty of ± 0.0001 in the g values, calculated for $g_e = 2.002319$ (Table 4 in ref. [45]),

^b In decalin or sucroseoctaacetate; ^cref. [46], ^dref. [47], ^eref. [48], ^fref. [49].

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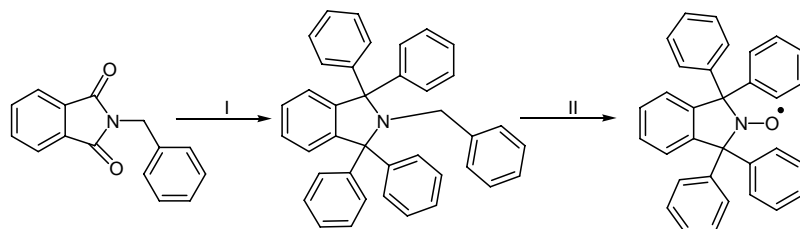
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Schemes



Scheme 1. – Synthetic Pathway for 1,1,3,3-tetraphenylisoindolin-2-yloxy (**TPHIO**).

(i) PhMgBr, toluene, reflux; (ii) MCPBA, DCM.

Figures.

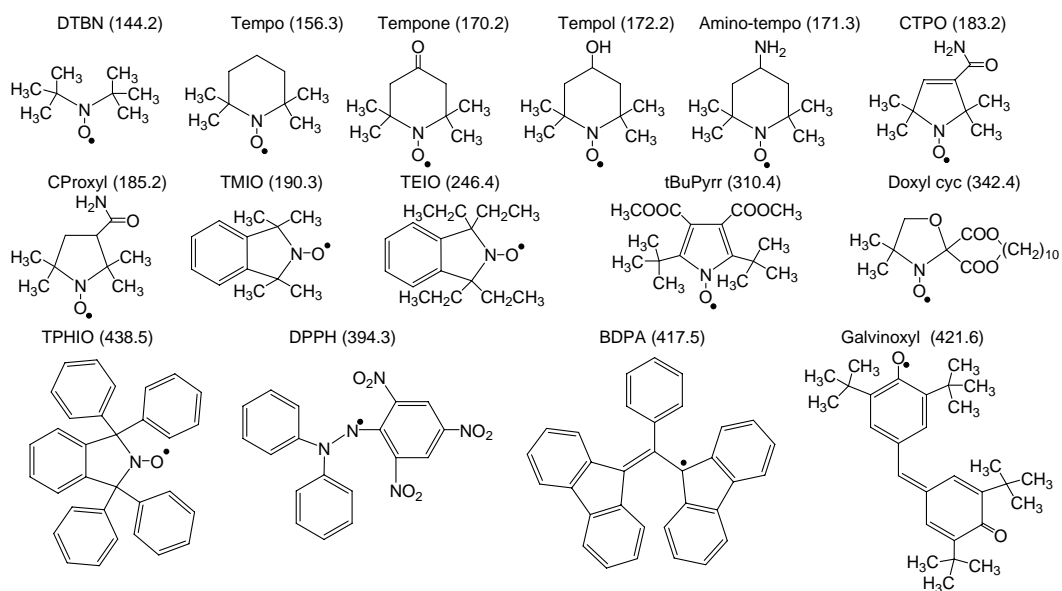


Figure 1. Structures and molecular weight of nitroxyls and other organic radicals examined in this study.

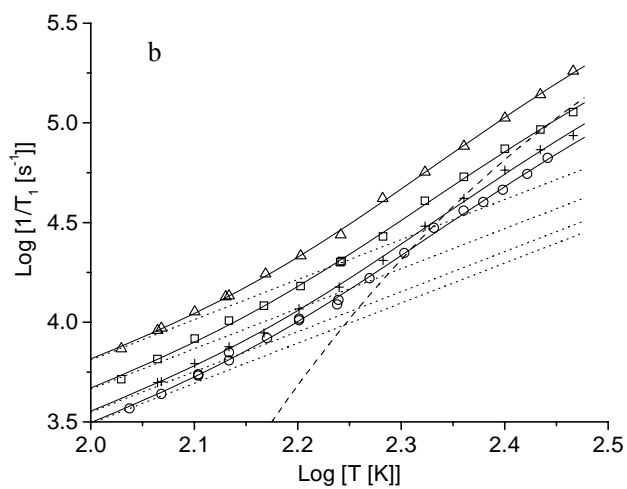
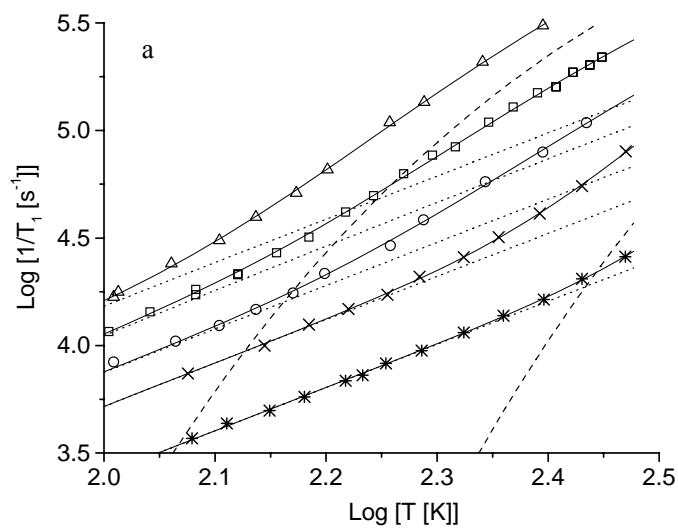


Figure 2. Temperature dependence of $1/T_1$ for nitroxyls in (a) sucrose octaacetate or (b) sorbitol; (Δ) DTBN, (\square) tempone, (\circ) CTPO, ($+$) tempol, (\times) TEIO and ($*$) TPHIO. The dotted and solid lines are the fits obtained using only the Raman process or the sum of contributions from the Raman process and additional process, respectively. The fit lines for the contribution from the additional process (---) are plotted for DTBN and TEIO in sucrose octaacetate and for DTBN in sorbitol.

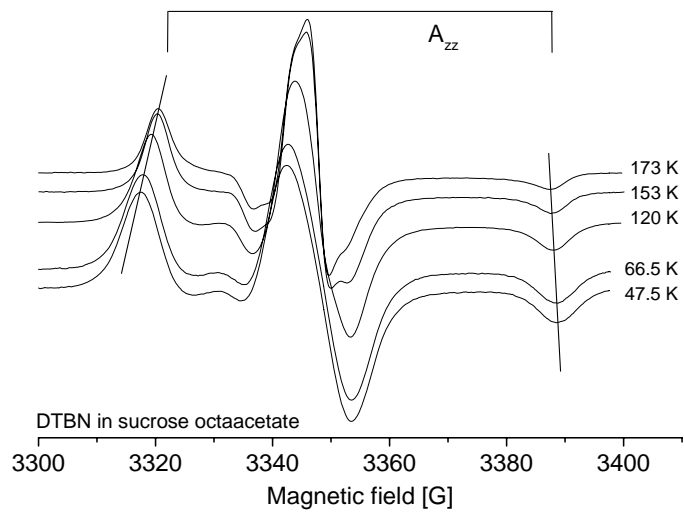


Figure 3. X-band CW EPR spectra of DTBN in sucrose octaacetate at several temperatures, showing the changes in A_{zz} .

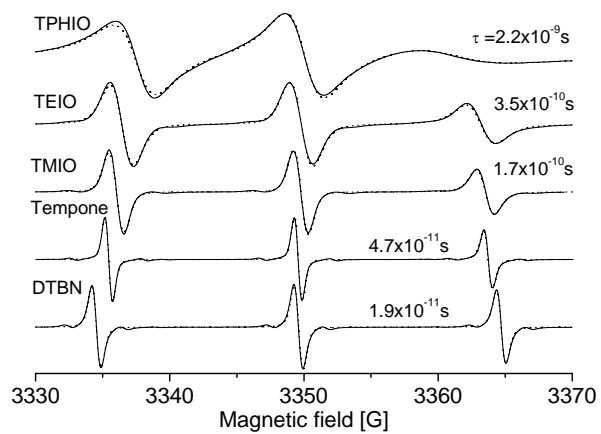


Figure 4. X-band CW EPR spectra of DTBN, tempone, TMIO, TEIO and TPHIO in decalin at 233 K and fit lines (- - -) calculated using the NLSL program [34].

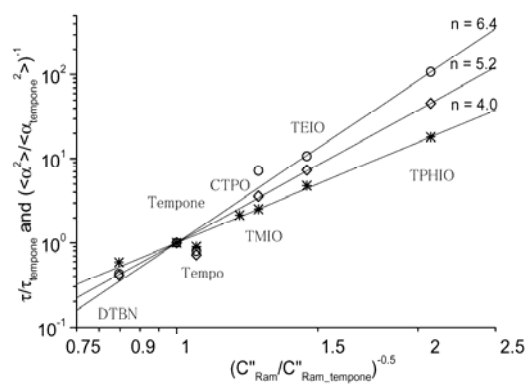


Figure 5. Comparison of the impact of molecular size on tumbling, libration, and the Raman coefficient. (*) $\langle \alpha^2 \rangle / \langle \alpha_{\text{temponc}}^2 \rangle^{-1}$ in sucrose octaacetate, $\tau / \tau_{\text{temponc}}$ in (◇) decalin and (○) heavy mineral oil as a function of $(C_{\text{Ram}}^n)^{-0.5}$. The solid lines are least-squares fits with slope = n.

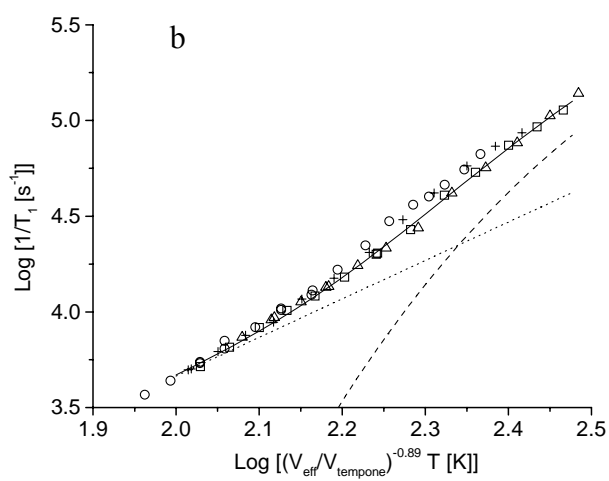
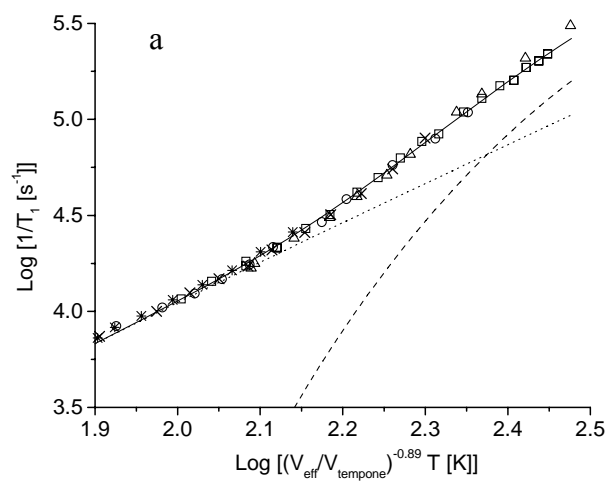


Figure 6. X-band spin-lattice relaxation rates, $1/T_1$, for nitroxyls in (a) sucrose octaacetate and, (b) sorbitol plotted as a function of $(V_{\text{eff}}/V_{\text{tempone}})^{-\gamma} T$; (Δ) DTBN, (\square) tempone, ($+$) tempol, (\circ) CTPO, (\times) TEIO and ($*$) TPHIO.

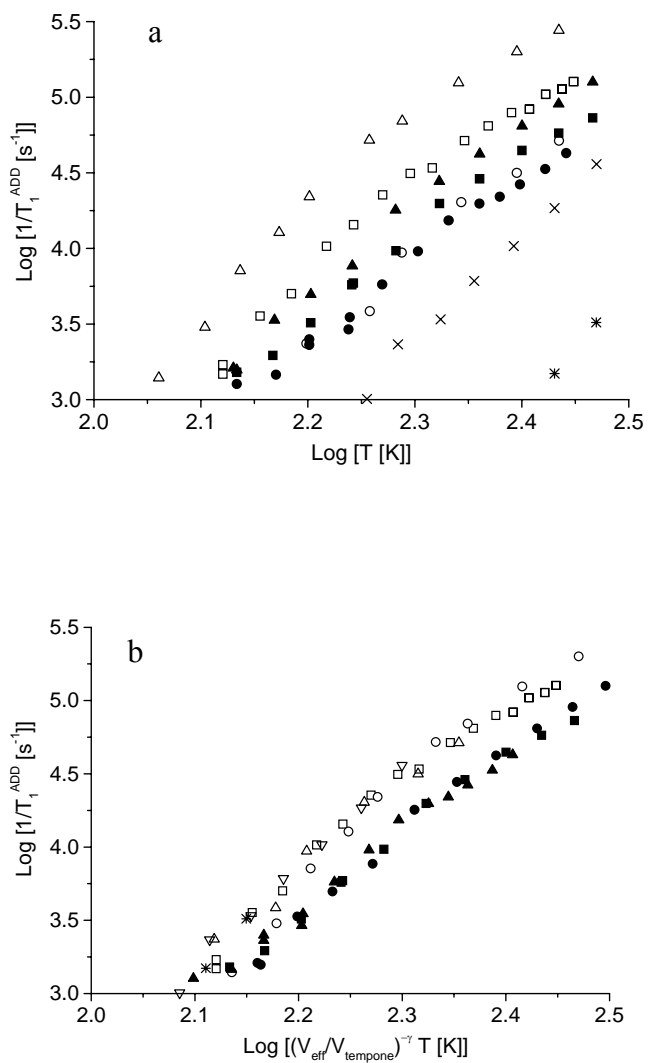


Figure 7. (a) Contribution to spin-lattice relaxation rates from the additional process, $1/T_1^{ADD}$ plotted as a function of $\log(T)$ and (b) $1/T_1^{ADD}$ plotted as a function of $\log(V_{\text{eff}}/V_{\text{tempone}})^{-\gamma} T$, for nitroxyls; (Δ) DTBN, (\square) tempone, (\circ) CTPO, (\times) TEIO and ($*$) TPHIO in sucrose octaacetate and (\blacktriangle) DTBN, (\blacksquare) tempone and (\bullet) CTPO in sorbitol.

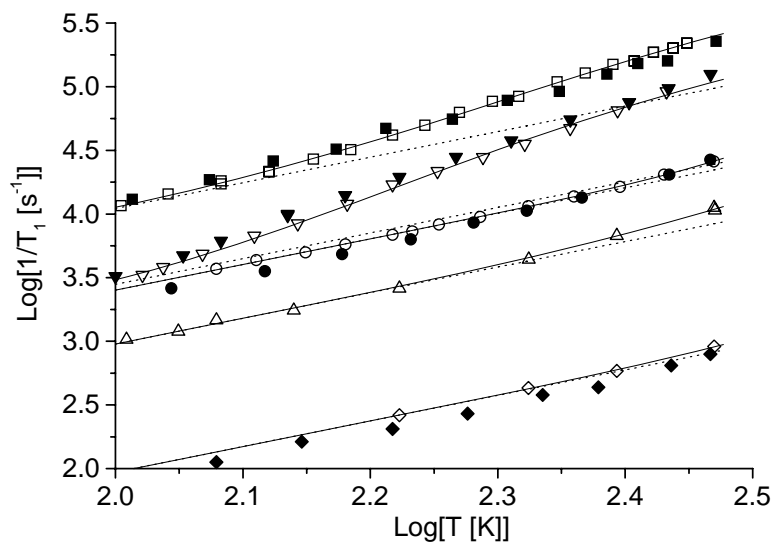


Figure 8. Spin-lattice relaxation rates, $1/T_1$, for organic radicals in sucrose octaacetate; (\square) tempone, (\circ) TPHIO, (\triangle) DPPH, (∇) galvinoxyl, and (\diamond) BDPA at X-band, and for (\blacksquare) tempone, (\bullet) TPHIO, (\blacktriangledown) galvinoxyl, and (\blacklozenge) BDPA at Q-band. The solid lines are fit lines for the combined impact of the Raman process and the additional process. The dashed lines show the contribution from the Raman process. Note that the dashed line for the contribution from the Raman process for galvinoxyl falls almost on top of the data points for TPHIO.

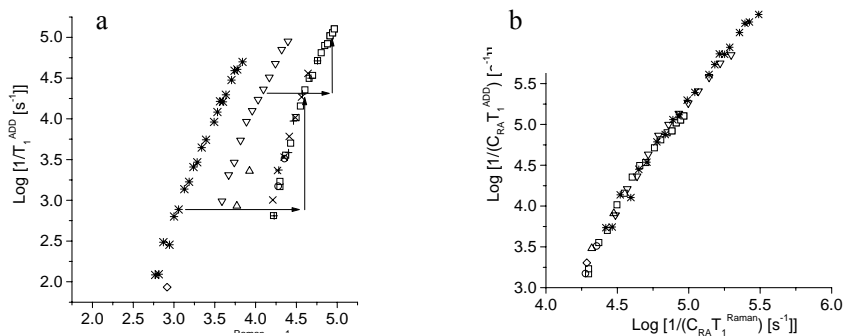


Figure 9. (a) Correlation between contributions to the relaxation rates from the Raman and additional process at X-band for nitroxyls (\square) tempone, (\times) TEIO, (\circ) TPHIO, (∇) galvinoxyl, (\triangle) DPPH, (\diamond) BDPA in sucrose octaacetate and ($*$) literature values for trityl- CD_3 radical in 1:1 water glycerol [50]. (b) Relaxation rates for the same samples replotted with both the x and y axes scaled by the same factor, C_{RA} . The arrows in (a) highlight the equal horizontal and vertical offsets that make the curves coincide.

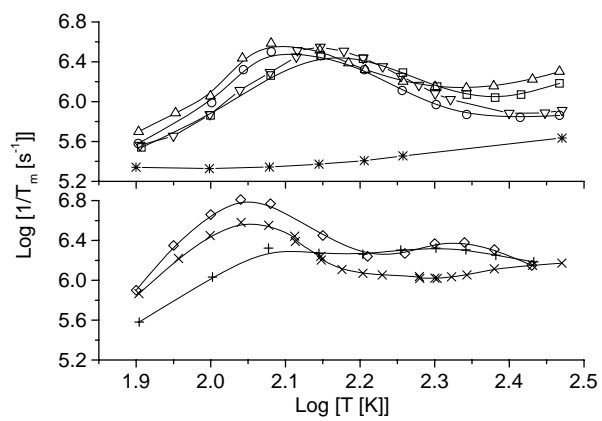


Figure 10. Temperature dependence of spin echo dephasing rates, $1/T_m$, in sucrose octaacetate for (Δ) DTBN, (\square) tempone, (\circ) CTPO, (∇) TMIO, (+) tBuPyrr, (\times) TEIO and ($*$) TPHIO and (\diamond) galvinoxyl.

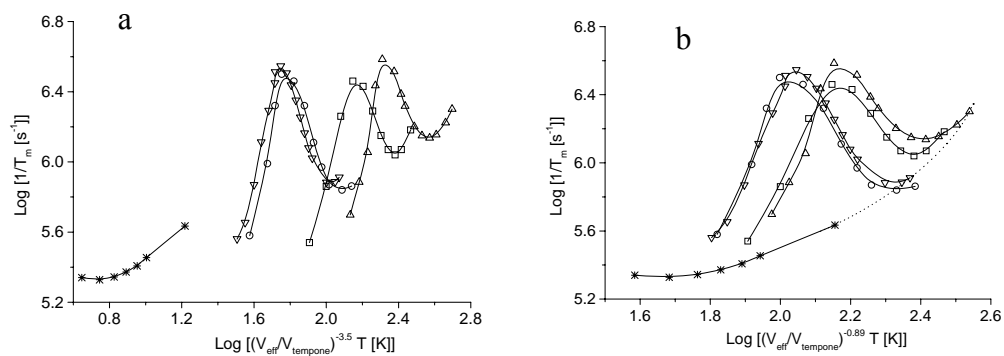


Figure 11. Spin echo dephasing rates for nitroxyls in sucrose octaacetate as a function of $(V_{\text{eff}}/V_{\text{tempone}})^{-\gamma} T$ using the values of $V_{\text{eff}}/V_{\text{tempone}}$ shown in Table 3 with (a) $\gamma = 3.5$ as observed for libration and (b) $\gamma = 0.89$ as observed for the Raman process; (Δ) DTBN, (\square) tempone, (\circ) CTPO, (∇) TMIO, and ($*$) TPHIO. The dashed line is an extrapolation of the temperature dependence for TPHIO, which is drawn for comparison with the higher-temperature points for the other nitroxyls.

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