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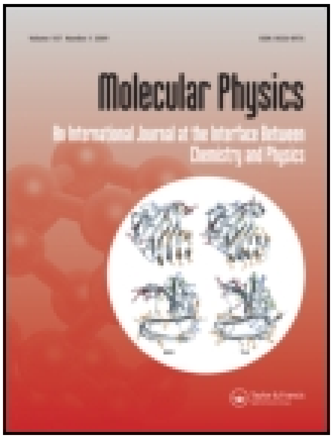

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Asymmetric line-width effects in the presence of resolved second order splittings: the E.S.R. spectra of 1,1-difluoroalkyl radicals in fluid solutions

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Asymmetric line-width effects in the presence of resolved second order splittings: the E.S.R. spectra of 1,1-difluoroalkyl radicals in fluid solutions

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The solution E.S.R. spectra of radicals of the type $R\dot{C}F_2$ exhibit marked line broadening attributable to rotational modulation of the ^{19}F anisotropic hyperfine interactions. This dipolar broadening is restricted to lines associated with the triplet state of the two equivalent ^{19}F nuclei and for slowly rotating radicals only the singlet state line is readily detectable.

1. INTRODUCTION

We have recently been interested in the E.S.R. spectra of radicals of the form $R\dot{C}F_2$ and in particular the α, α-difluorobenzyl radical (R = Ph). We therefore irradiated with ultra-violet light a mixture of triethylsilane, di-*t*-butyl peroxide and $C_6H_5CF_2Cl$ in the cavity of a Varian E3 spectrometer expecting to see $C_6H_5\dot{C}F_2$ radicals produced by the reaction sequence

$$Bu^tO{\cdot}OBu^t \xrightarrow{h\nu} 2Bu^tO.$$

$$Bu^tO\cdot + HSiEt_3 \rightarrow Bu^tOH + Et_3Si.$$

$$Et_3Si\cdot + C_6H_5CF_2Cl \rightarrow Et_3SiCl + C_6H_5CF_2.$$

This procedure has previously been successfully used to prepare a variety of radicals from alkyl chlorides or bromides [1] including the pentafluorobenzyl radical $C_6F_5\dot{C}H_2$. When $C_6H_5CF_2Cl$ was used as a substrate at $-60°$ a well-resolved E.S.R. spectrum was observed which could be analysed in terms of triplet splittings of 5·07 G and 1·73 G and a 5·83 G doublet. These coupling constants are of the magnitude expected for the ring protons of a benzyl radical; benzyl itself has $a_H{}^{0} = 5{\cdot}14$, $a_H{}^{m} = 1{\cdot}75$ and $a_H{}^{p} = 6{\cdot}14$ G. There was not however any splitting attributable to the two fluorine nuclei. We present evidence in this paper to suggest that the observed spectrum is to be associated with the singlet spin state ($k = 0$) of the two equivalent fluorine nuclei and that the remaining lines associated with the triplet ($k = 1$) state are unobservably broad at the radical concentrations involved. To investigate further the line broadening in 1,1-difluoroalkyl radicals we have also made measurements on the species $\dot{C}F_2COOH$ and $\dot{C}F_2H$ which have been previously studied in rigid matrices and have simpler E.S.R. spectra than $C_6H_5\dot{C}F_2$. Because of the magnitude of the fluorine coupling constants, these systems provide a unique opportunity to study line-widths in the presence of resolved second order splittings.

2. THEORY

We consider a radical $R\dot{C}F_2$ in which the unpaired electron interacts with two equivalent ^{19}F nuclei. The static spin hamiltonian is

$$\hbar\mathscr{H}_0 = g\beta HS_z + ha\mathbf{S} \cdot (\mathbf{I}_1 + \mathbf{I}_2) \qquad (1)$$

and since we expect a to be quite large (84·2 G for CHF_2) it is necessary to include second order terms in evaluating the line positions. As has been shown by Fessenden [2] it is advantageous to work in a coupled representation for the nuclear spins ; in the present case this gives rise to triplet and singlet states with total nuclear spin angular momenta $k = 1$ and $k = 0$ respectively. The spin hamiltonian then takes on a block diagonal form and to second order the line positions are given by [2] :

$$\nu_0 = \nu_e + k_z a + (a^2/2\nu_0)(k^2 + k - k_z^2), \qquad (2)$$

where $\nu_e = g\beta H_0/h$ is the position of the centre of the spectrum. For the $k = 0$ state $\nu_0 = \nu_e$; for the triplet $k_z = 0$ gives $\nu_0 = \nu_e + a^2/\nu_0$ and $k_z = \pm 1$ gives $\nu_0 = \nu_e \pm a + a^2/2\nu_0$. The second order splitting of the $k_z = 0$ components of the first order triplet is therefore a^2/ν_0, or, taking $a = 80$ G and $H_0 = 3300$ G, *circa* 2 G. A splitting of this magnitude should be easily resolvable in the solution spectra of 1,1-difluoroalkyl radicals.

To account for line-width variations between the various second order components we need to consider possible relaxation mechanisms. Modulation of the anisotropic g and hyperfine tensors by rotational brownian motion is usually the most important line broadening mechanism for organic radicals in solution and the theory is well understood [3–5]. The situation we are concerned with is particularly simple ; because all the lines are well resolved and non-degenerate there is just a single relaxation matrix element for each line.

We have already noted that the two ^{19}F nuclei are equivalent (i.e. they have identical isotropic hyperfine coupling constants) and for simplicity we shall further assume that they are completely equivalent and also have identical hyperfine tensors. A survey of single crystal results on $R\dot{C}F_2$ radicals [6–8] shows that ^{19}F hyperfine tensors are essentially axially symmetric with the major principal axis perpendicular to the C–F bond. The time-dependent perturbing hamiltonian which gives rise to relaxation can then be written as

$$\mathscr{H}(t) = \mathscr{H}(\mathbf{k}, \mathbf{S}) + (\text{small})\mathscr{H}(\mathbf{I}_1 - \mathbf{I}_2, \mathbf{S}) \qquad (3)$$

and the assumption of complete equivalence is quite reasonable. It follows that groups of hyperfine levels with different eigenvalues of k^2 and k_z relax independently [3, 4]. The line-widths are given by :

$$\begin{aligned} T_2^{-1} = {} & (1/60)(T:T)\{(3k(k+1) + 5k_z^2)J_0 + (7k(k+1) - k_z^2)J_1\} \\ & + (1/30)(4J_0 + 3J_1)\{(2\beta H/\hbar)(T:g)k_z + (\beta H/\hbar)^2(g:g)\}, \end{aligned} \qquad (4)$$

where $(T:T)$, $(T:g)$ and $(g:g)$ are inner products of the anisotropic hyperfine and g-tensors, $J_0 = \tau_2$ (the correlation time for the molecular motion) and $J_1 = \tau_2/1 + \omega_0^2\tau_2^2$.

The g-tensor anisotropy is expected to be small for the radicals of interest. Furthermore we note that the term involving $(g:g)$ contributes equally to all the hyperfine lines and the term in $(T:g)$ is zero for $k_z=0$. We are mainly interested in the relative widths of the two $k_z=0$ lines and therefore ignore terms in (4) involving g. We then obtain the dipolar contributions to T_2^{-1} in table 1. The singlet state line is unaffected by the dipolar mechanism but all the triplet state lines are broadened ; the widths should be greatest for the $k_z=\pm 1$ components. This result is in fact well known ; if the nuclei are completely equivalent the relaxation matrix is diagonal even if the $k_z=0$ components are degenerate. Indeed the most important result of applying Redfield's relaxation matrix theory to E.S.R. line widths is the realisation [3] that a composite line arising from a set of degenerate nuclear spin states consists, in general, of a sum of lorentzians with different widths. The overall line shape is not necessarily lorentzian. Experimentally this situation has been extensively investigated in connection with the alternating line-width effect [5]. However, in investigations of asymmetric line-width effects in organic radicals [5, 9, 10], it has usually been the case that the line-width variations are small. The line shape can then be approximated by a single lorentzian with an average width [3, 4]. In their study of the N,N′-dimethylpyrazine cation, Ahn and Johnson [10] made corrections for the effects of poorly resolved second-order splittings on the measured line widths but used a single width for all the components of a hyperfine line. In the radicals studied in the present work the second-order splittings are well resolved and therefore present a unique opportunity for studying the variations in component line widths predicted in table 1.

k	k_z	T_2^{-1}
1	± 1	$(1/60)(11J_0+13J_1)(T:T)$
0	0	$(1/60)(6J_0+14J_1)(T:T)$
0	0	0

Table 1. Dipolar contributions to the line-widths for two completely equivalent $I=\frac{1}{2}$ nuclei.

3. Experimental

All the radicals were prepared by extraction of chlorine from an appropriate halide using the sequence of reactions outlined in the introduction [1]. Chlorodifluoroacetic acid and chlorodifluoromethane were obtained commercially and used without further purification. $C_6H_5CF_2Cl$ was prepared from $C_6H_5CCl_3$ and Na_2SiF_6 as described by Dahmlos [11]. The procedures used for measuring the E.S.R. spectra and sample temperatures have been reported [12]. The solution used in the variable temperature study of the $\dot{C}HF_2$ radical was prepared on a vacuum line by condensing a small amount of CHF_2Cl into a mixture containing two parts of triethylsilane to one part of di-*t*-butyl peroxide. The final mixture contained about 10 per cent by volume of CHF_2Cl.

4. Results

As mentioned in the introduction, at −60° the E.S.R. spectrum attributed to $C_6H_5\dot{C}F_2$ showed all the expected proton splittings but no triplet from the two fluorine nuclei. This can be understood if the broadening of the $k=1$ lines is sufficient to render them unobservable. We attempted to sharpen these lines by raising the temperature and hence shortening the rotational correlation time but this gave lower radical concentrations and poorer spectra. The $C_6H_5\dot{C}F_2$ spectrum is quite complicated and there are obvious advantages in choosing a simpler system; we therefore turned our attention to the radical $\dot{C}F_2COOH$. The related species $\dot{C}F_2COO^-$ has recently been reported in irradiated single crystals of sodium chlorodifluoroacetate [8]. At $-60°$ the reaction of triethylsilyl radicals with chlorodifluoroacetic acid gave a single sharp line in the E.S.R. spectrum. Similar results were obtained at room temperature but at 50°C we observed the spectrum shown in figure 1. All the expected lines are detectable and the preferential broadening of the $k=1$ components is clearly established. Furthermore the $k_z=\pm 1$ components of the triplet state are broader than the $k_z=0$ component as predicted. The fluorine coupling constant of 64 G is comparable with the values of 68·8, 69·7 and 72·4 G found for the three sets of $\dot{C}F_2COO^-$ radicals in irradiated $CClF_2COONa\,.\,2H_2O$ [8]. Unfortunately the radical concentration decreased rapidly at 50°C and it was not possible to extend the observations to higher temperatures and observe a further sharpening of the $k=1$ lines. We were however able to obtain spectra over a wider range of temperature for the radical $\dot{C}HF_2$.

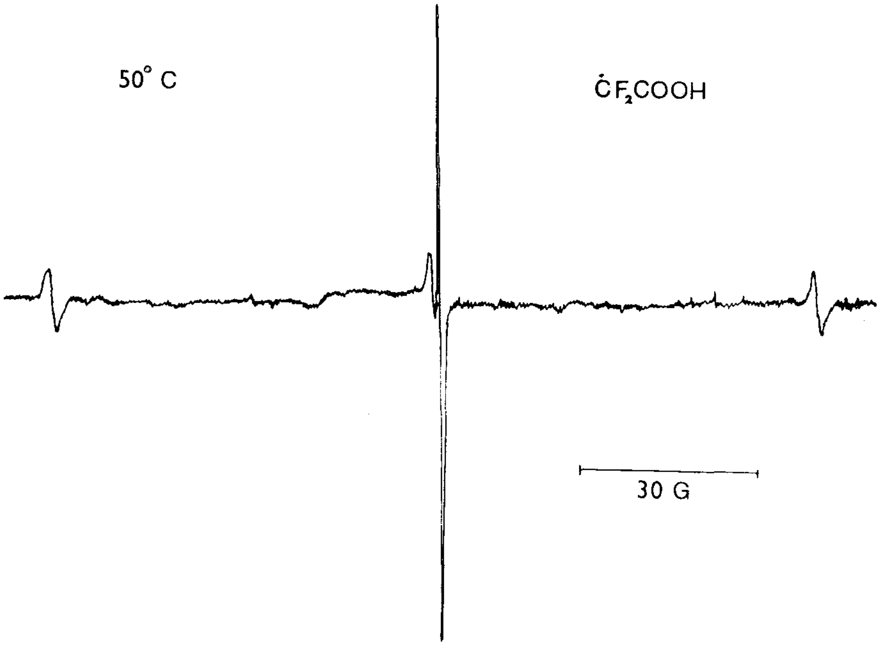

Figure 1. The E.S.R. spectrum of $\dot{C}F_2COOH$ at 50°C.

The difluoromethyl radical has been previously reported by Fessenden and Schuler [13] who irradiated a 2 per cent solution of CH_2F_2 in a Xe matrix at -188°C. An isotropic spectrum was observed with $a_F=84{\cdot}2$ G, $a_H=22{\cdot}2$ G, $a_{^{13}C}=148{\cdot}8$ G, and $g=2{\cdot}0041$. The radical is non-planar and the proton splitting is positive [14]. We have prepared $\dot{C}HF_2$ from CHF_2Cl and observed its E.S.R. spectrum from −110° to −40°C. Over this temperature range we found no dependence of the line-widths on the proton nuclear spin quantum number and we shall ignore the proton in what follows. We also found that the outer $k_z = \pm 1$ lines had essentially identical widths thus justifying the neglect of the term involving $(T:g)$ in equation (4). The temperature dependence of the line widths for the $k_z = 0$ peaks is shown in figure 2. At −97°C the singlet state line is considerably sharper than the triplet component but at −40° the two lines have nearly equal widths. It is noticeable however that the singlet line gets broader as the temperature is raised whereas we might have expected it to remain sharp and for the triplet line to sharpen. As we shall show later it is probable that this increase in the non-dipolar part of the line-width is due to spin-rotational interactions [5, 15–17]. The line-width variations follow qualitatively the behaviour predicted in § 2. In the next section we shall attempt a more quantitative treatment of the results and for this we require to measure the line widths.

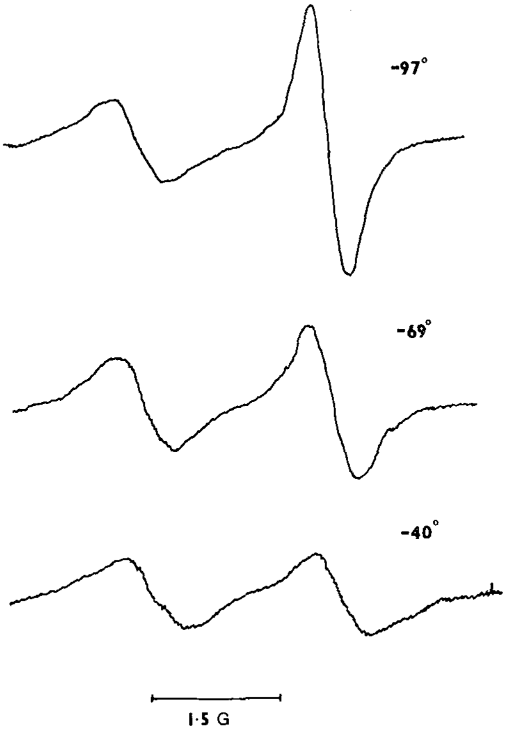

Figure 2. Temperature dependent variations in the widths of the second order components of the $k_z = 0$ line in the E.S.R. spectrum of $\dot{C}HF_2$.

Careful line-width studies have generally been performed on solutions of stable radical ions [5, 9, 10]. Since we are dealing with short lived radicals which are only detectable using high amplifier gain the accuracy of our measurements is inevitably lower. It was not possible to observe spectra with the modulation amplitude reduced to a level at which distortion of the line shape could be ignored and values of T_2^{-1} were determined from traces recorded on an expanded scale and corrected for modulation broadening using standard procedures [18]. The results of measurements at −169° and −82° are given in table 2. At −40° all the lines have approximately the same width of 0·5 G. We estimate that the values in table 2 are accurate to ± 10 per cent.

Temp.	k	k_z	T_2^{-1} (G)	Dipolar contribution
−106°	0	0	0·28	0
	1	0	0·39	0·11
	1	±1	0·41	0·13
−82°	0	0	0·37	0
	1	0	0·43	0·06
	1	±1	0·47	0·10

Table 2. Results of line-width measurements for $\dot{C}HF_2$.

5. Calculation of the line widths

We can calculate the dipolar contributions to the line widths as a function of τ_2 if we know the anisotropic hyperfine tensor. Unfortunately this is not available for $\dot{C}HF_2$ but is known for related radicals such as $\dot{C}F_2COO^-$ and $\dot{C}F_2CONH_2$ [6–8]. Consideration of the available data on α-fluorine hyperfine tensors suggests that no serious errors are introduced by assuming axial symmetry and taking the principal component of the tensor to be 350 MHz. We then calculate the line-width contributions shown in figure 3. For very short correlation times $J_0 = J_1$ and the widths of the $k_z = 1$ and $k_z = 0$ lines should be in the ratio 1·2 : 1. Experimental values for the dipolar contributions obtained by subtracting the width of the $k = 0$ line are listed in table 2. At −106° the ratio of the dipolar contributions for $k_z = 1$ and $k_z = 0$ is 1·18 : 1 in excellent agreement with the predicted value. At −82° the ratio of 1·6 : 1 is less satisfactory and probably reflects the poorer signal to noise found at higher temperatures. The corresponding values of τ_2 are $0·8 \times 10^{-12}$ sec at −106° and $0·5 \times 10^{-12}$ sec at −82°. These correlation times are typical of those found for small molecules in liquids from the measurement of nuclear relaxation times or the Fourier inversion of vibrational band contours [19].

Although the dipolar mechanism accounts for differences between the widths of the $k = 0$ and $k = 1$ lines in the E.S.R. spectrum of $\dot{C}HF_2$, it does not account for all the observed line widths. Moreover the observed line widths increase with temperature although the dipolar contributions decrease. At −40° the latter become negligible and the lines have the same width of *circa* 0·5 G. This behaviour is typical of spin-rotational relaxation [15–17]. By making a number of assumptions we can obtain an estimate of the spin-rotational contribution to the line widths. For a radical with cubic symmetry undergoing isotropic rotational diffusion [16] :

$$T_2^{-1} = (\Delta g : \Delta g)/9\tau_2. \tag{5}$$

The g-tensor of $\dot{C}HF_2$ is unknown but for $\dot{C}F_2COO^-$ [8] the principal components on 2·0031, 2·0047 and 2·0040 ; the average value of 2·0039 is close to the g-factor of 2·0041 reported for $\dot{C}HF_2$ [13]. Using these values and equation (5) together with the values of τ_2 calculated earlier, we estimate line width contributions of 0·07 G at −106° and 0·12 G at −82°. The results are of the right order of magnitude but are somewhat smaller than the observed residual line widths. This is not unexpected as it is well known that the motion of small molecules is not adequately described by a rotational diffusion model. This problem has been investigated in detail by Kivelson and co-workers [17, 20]. Nevertheless the level of agreement is sufficient to justify our assignment of the line widths at high temperatures to a spin-rotational mechanism.

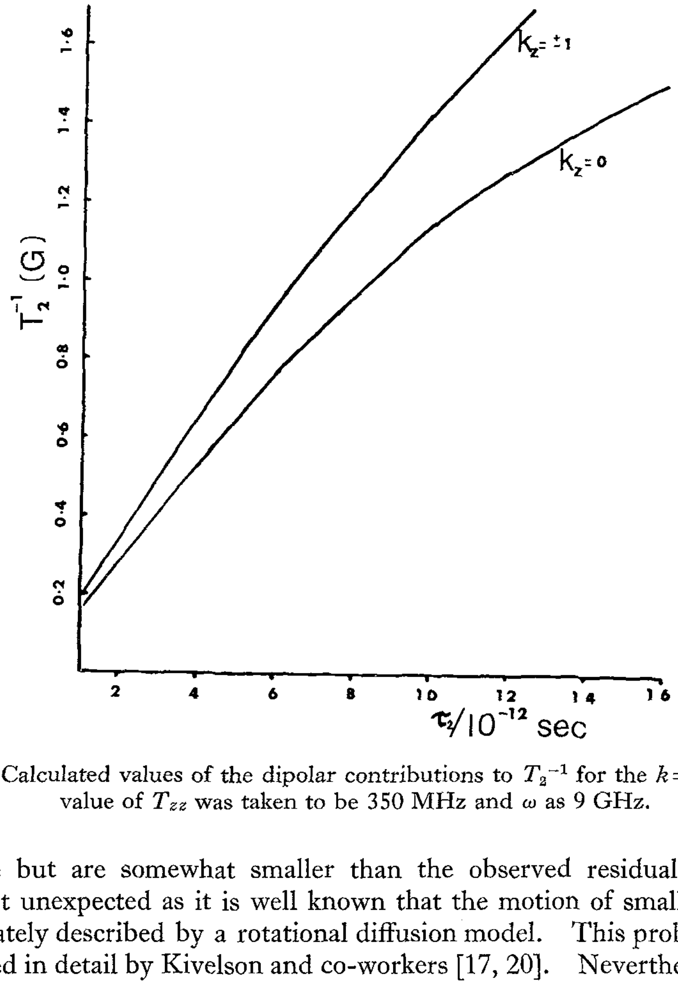

Figure 3. Calculated values of the dipolar contributions to T_2^{-1} for the $k=1$ lines. The value of T_{zz} was taken to be 350 MHz and ω as 9 GHz.

6. Conclusions

1,1-Difluoroalkyl radicals exhibit large asymmetric line-width effects which have been shown to arise principally from rotational modulation of the ^{19}F anisotropic hyperfine interaction. For a small radical such as $\dot{C}HF_2$ it is still possible to observe all the E.S.R. lines but for larger radicals, with longer rotational correlation times, the lines associated with the triplet state of the two fluorine nuclei may be unobservably broad.

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