

Letters to the Editor

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Nuclear Magnetic Spin-Lattice Relaxation in Liquids*

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WE have measured the proton and fluorine T_1 's in CH_2FCl , CHF_2Cl , CHFCl_2 , and 1,3,5-trifluorobenzene at room temperature using the spin-echo method of two 90° pulses.¹ The molecular structures are such that, according to the usual relaxation models for liquids,²⁻⁵ the direct magnetic dipole-dipole interactions are nearly identical for protons and fluorines in the same molecule and therefore so should be the T_1 's. However, the observed proton T_1 's, given in Table I, are several times longer than the corresponding fluorine T_1 's. Anisotropy of the fluorine chemical shift⁶ explains⁷ the results for 1,3,5-trifluorobenzene but it is not the dominant factor for the Freons.

The intramolecular and translational dipole-dipole contributions to T_1 were calculated as^{2,3}

$$(1/T_1)_{\text{intra}} = \hbar^2 \gamma_i^2 \left(\frac{2}{3} \gamma_i^2 \sum_j r_{ij}^{-6} + \gamma_f^2 \sum_f r_{if}^{-6} \right) \tau_c, \quad (1)$$

$$(1/T_1)_{\text{trans}} = (\pi^2 \hbar^2 \gamma_i^2 \eta N a / kT) \left[3 \gamma_i^2 \sum_j (1/r_{ij}^6) + 2 \gamma_f^2 \sum_f (1/r_{if}^6) \right], \quad (2)$$

using $\tau_c = 4\pi\eta a^3 / 3kT$. The molecular radius a was estimated from the molar volumes; r^0 , the distance of closest approach of nuclei in different molecules, was taken to be $2a$. For typical fluorocarbons the viscosity η is about 5×10^{-3} , which gives proton T_1 's in CHFCl_2 and 1,3,5-trifluorobenzene of 10.5 and 11.5 sec in fair agreement with experiment. The viscosity effects cancel upon taking the ratio of T_1 's, which are included in Table I. The experimental ratios are from 1.7 to 9 times

as large as those computed. No significant improvement has been obtained by reasonable adjustment of the parameters available in this model.

Anisotropy in the chemical shift tensor σ produces in the laboratory xy plane, at the nucleus, a magnetic field H_σ which, for a nucleus surrounded by an electron distribution that is axially symmetric about the z' axis, is

$$H_\sigma = (\sigma_{zz}^2 + \sigma_{yy}^2)^{1/2} H_z = \sin\theta \cos\theta (\sigma_{zz}' - \sigma_{xx}') H_0. \quad (3)$$

The x and y components of H_σ are $-H_\sigma \cos\phi$ and $H_\sigma \sin\phi$. θ and ϕ give the orientation of the molecular axes, x' , y' , z' , with respect to the laboratory system, x , y , z . Molecular reorientations produce fluctuations in the field which contribute a term to T_1 , calculated by the methods of Bloembergen, Purcell, and Pound² to be⁷

$$(1/T_1)_\sigma = (2/15) \gamma^2 H_0^2 (\sigma_{zz}' - \sigma_{xx}')^2 \tau_c / (1 + \omega_0^2 \tau_c^2). \quad (4)$$

If $\omega_0^2 \tau_c^2 \ll 1$, as was true in these experiments, then $(1/T_1)_{\text{dipolar}}$ is independent of H_0 whereas $(1/T_1)_\sigma$ increases as H_0^2 , so that $(1/T_1)_\sigma$ can be deduced from the field dependence of $(1/T_1)_{\text{obs}}$.

The proton shifts are too small for their anisotropy to be important here. The proton T_1 's in Table I vary at random while the fluorine T_1 's are consistently shorter at the higher field. Calculation of the fluorine shift anisotropy from the field dependence is complicated by the lack of reliable values for τ_c . The procedure adopted was to fit the T_1 ratios by $R = R_0 + AH_0^2$, which gives $A = (2/15) \gamma_f^2 (\sigma_{zz}' - \sigma_{xx}')^2 \tau_c T_{1H}$. Equations (1) and (2) were then used to eliminate $\tau_c T_{1H}$. The data for 1,3,5-trifluorobenzene are the most reliable, giving $(\sigma_{zz}' - \sigma_{xx}') = 7.5 \times 10^{-4}$, which is also the average anisotropy from the Freons. This result supports the conclusion⁸ that the fluorine shifts arise in main from the second-order paramagnetism of the covalent p electron. For such a p electron, we find $\sigma_{zz}' = 0$; moreover, $\sigma_{zz} = \sigma_{xx}' \sin^2\theta + \sigma_{zz}' \cos^2\theta$, and, finally, $\langle \sigma_{zz} \rangle_\lambda = \frac{2}{3} \sigma_{xx}'$. The observed shift,⁹ $\langle \sigma_{zz} \rangle_\lambda$, for a C-F fluorine, attributable to the covalent p electron is 6.5×10^{-4} which is about $\frac{2}{3}$ of the observed anisotropy as predicted by the model.

At present we have no good explanation of the large T_1 ratios for the Freons. There is an indirect proton-fluorine coupling of about 10 cps in the compounds, but this seems too small for its anisotropy or other effects³⁻⁵ to be significant. Dissolved oxygen was re-

TABLE I. Proton and fluorine spin-lattice relaxation times in molecular liquids at room temperature.^a

Compound	Proton T_1		Fluorine T_1		$R = T_{1H}/T_{1F}$		Dipolar
	20 Mc/sec	26.5 Mc/sec	20 Mc/sec	26.5 Mc/sec	20 Mc/sec	26.5 Mc/sec	
CH_2FCl	34.6 ± 1.0	34.4 ± 0.7	9.11 ± 0.05	8.69 ± 0.05	3.80 ± 0.12	3.96 ± 0.08	0.44
CHFCl_2	46.9 ± 0.2	42.1 ± 0.7	5.10 ± 0.08	4.76 ± 0.14	9.20 ± 0.15	8.85 ± 0.35	0.98
CHF_2Cl	6.3 ± 0.1	6.73 ± 0.14	1.77 ± 0.01	1.69 ± 0.05	3.56 ± 0.08	3.98 ± 0.14	0.88
$\text{C}_6\text{H}_3\text{F}_3^b$	26.0 ± 0.4	26.7 ± 0.7	16.7 ± 0.1	15.6 ± 0.15	1.56 ± 0.02	1.71 ± 0.06	0.93

^a T_1 is given in seconds; the errors are probable errors.

^b 1,3,5-trifluorobenzene.

moved from the samples; it does not appear to have a differential effect. For a sample of 1,3,5-trifluorobenzene containing oxygen, T_{1H} and T_{1F} were 1.85 and 1.82 sec at 20 Mc/sec. Further work is in progress on the problem and also on the chemical shift anisotropy. We wish to thank A. Saika and G. A. Williams for several helpful discussions and E. O. Stejskal for assistance with the measurements.

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Transmission of Superconducting Films at Millimeter-Microwave and Far Infrared Frequencies*

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MEASUREMENTS of the surface resistance of superconductors at microwave frequencies having photon energy comparable with kT_c have recently been announced. For tin¹ these measurements have been carried up to a frequency corresponding to $h\nu = 1.9kT_c$ and for aluminum² to $2.3kT_c$. At these frequencies and at the lowest temperatures tried, both materials lost part but not all of their resistance in the superconducting state. At considerably higher frequencies, the absorption coefficient of tin has been studied.³ For $\lambda = 0.014$ mm, corresponding to $275kT_c$, no change in the absorption between normal and superconducting states was found, indicating no change in the resistance. We have made measurements of the transmission through superconducting lead and tin films. The frequencies used cover a good part of the previously unexplored intermediate region.

The quantity measured experimentally is the ratio of power transmitted through the film in the superconducting state to that in the normal. In Fig. 1 this is plotted against frequency for a typical lead film. Both the low-energy points, which indicate a reduction of the transmission corresponding to a partial loss of resistance in the superconducting state, and those at high energies for which there is no change, are in qualitative agreement with the previous experiments

on bulk material. The high-energy data now make it possible to fix the maximum frequency for which there is a difference between the normal and superconducting states at about $20kT_c/h$. The most striking aspect of the results is that over a considerable region of frequencies the superconducting film has a higher transmission, corresponding roughly to *higher* resistance, than the normal film. The frequency dependence of Sn films has been measured only approximately. The existence of a maximum also in the transmission for Sn has been verified. If the frequency scale is reduced in the ratio of the transition temperatures ($3.7/7.2 \sim 0.5$), the results seem consistent with those for Pb. A suggested interpretation of the data is given by one of us in a separate letter.⁴ Our results appear to support the energy-gap model of superconductors.

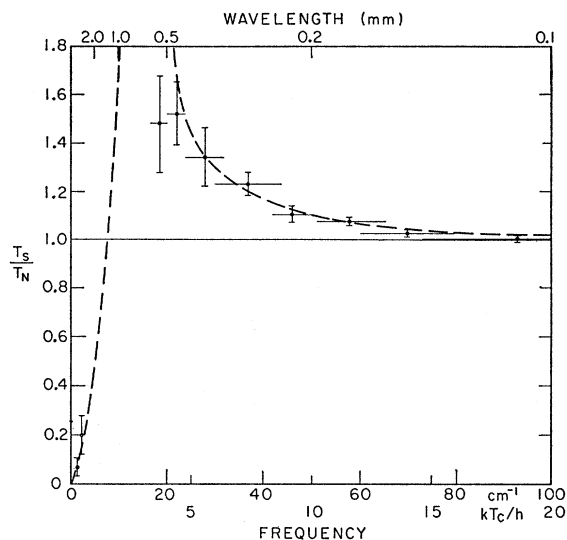


FIG. 1. Experimental transmission ratios of superconducting and normal states of a typical lead film (dc residual resistance 117 ohms; transmission in normal state = $\frac{1}{4}$) at $T/T_c = 0.67 \pm 0.03$. The frequency uncertainty on each infrared point is the half-power width of the continuous spectrum used. The vertical error limits on these points are derived statistically from the data. The dashed curve is one proposed for $T=0$ and an energy gap of $3kT_c$, as described in the following Letter.

Films were produced *in situ* by evaporation in high vacuum onto a crystal quartz substrate held at 77°K and were annealed at room temperature. Current and potential contacts made it possible to monitor the dc resistance. Superconductivity could be destroyed by exceeding a critical value of the current. Estimates made both from the temperature-dependent part of the resistance and from the Fuchs⁵ theory, assuming diffuse surface scattering, indicate that the thickness of the Pb film used was ~ 20 Å. (Sn films up to five times as thick were also tried; all showed the increase in transmission.) The critical temperature was 0.12°K lower than for bulk material. The width of the transition region was less than 0.1°K.