

plot and  $p(\text{F}_2)$  and  $p(x)$  are the pressures of fluorine and added gas, respectively, and  $\delta(\text{F}_2)$  and  $\delta(x)$  the broadening coefficients. Thus, a plot of  $\Delta H/p(x)$  vs  $p(\text{F}_2)/p(x)$  will yield  $\delta(x)$  as the intercept and  $\delta(\text{F}_2)$  as the slope. Such a plot for a large number of runs of the (1, 1 $\rightarrow$ 1, 0) transition of atomic fluorine gave  $\delta(\text{F}_2) = 1.0$ ,  $\delta(\text{Ar}) = 0.5$ , and  $\delta(\text{He}) = 0.7$  G/torr. These observed linewidths can be related to the collision cross sections in the usual manner.<sup>1</sup> In the calculations it has been assumed that the F-atom concentration is sufficiently low that the contribution to the width from F-F collision can be neglected. In a large number of runs in which the F-atom concentration was measured as a function of position along the flow tube we were never able to detect any variation in linewidth although the fluorine atom concentrations varied by two orders of magnitude.

The broadening cross section derived from the linewidth data are given in Table I. For atomic fluorine the  $g$  value was taken as 1.33. Although the effect of foreign gas broadening was not examined in detail for the other lines, sufficient data were obtained to make some comparisons. The width (1, 1 $\rightarrow$ 1, 0) transition (the center line of the low field triplet) was identical to that of the (2, 0 $\rightarrow$ 2, -1) line. However, the width of the other transitions was significantly larger. For a run with 1.38 torr of  $\text{F}_2$  in 11.40 torr of He, the average width for the two center lines (corresponding to the  $M_J - \frac{1}{2} \rightarrow \frac{1}{2}$  strong field transitions) was 6.59 G while for the other ( $\frac{1}{2} \rightarrow \frac{3}{2}$  and  $-\frac{3}{2} \rightarrow -\frac{1}{2}$ ) transitions the average width was 9.34 G. The integrated intensities of these lines were in the ratio 1.288 in good agreement with the theoretical factor of 1.3. A similar observation<sup>1</sup> has been reported for Cl where the width of the  $M_J - \frac{1}{2} \rightarrow \frac{1}{2}$  transition also was significantly lower than the others.

In the case of I atoms observations were limited to the  $M_J - \frac{1}{2} \rightarrow \frac{1}{2}$  line at approximately 4950 G ( $\nu = 9274$  MHz). As in the case of fluorine, for constant  $\text{I}_2$  pressure the linewidth was independent of the I concentration. From the variation of width with  $\text{I}_2$  pressure over the range 0.01-0.3 torr a broadening coefficient of 2.4 G/torr was obtained. From this the cross section for

TABLE I. Collision cross section for line broadening.

Species	Cross section ( $\text{cm}^2 \times 10^{14}$ )	Reference
O( $^3P_2$ )-O <sub>2</sub>	0.45	6
O( $^3P_1$ )-O <sub>2</sub>	0.37	1
F( $^3P_{3/2}$ )-F <sub>2</sub>	0.44	This work
F( $^3P_{3/2}$ )-He	0.16	This work
F( $^3P_{3/2}$ )-Ar	0.51	This work
Cl( $^3P_{3/2}$ )-Cl <sub>2</sub>	0.71	5
Cl( $^3P_{3/2}$ )-Ar	0.32	1
I( $^3P_{3/2}$ )-I <sub>2</sub>	2.8	This work
I( $^3P_{3/2}$ )-He	0.32	This work
I( $^3P_{3/2}$ )-Ar	0.51	This work

broadening of I by  $\text{I}_2$  was found to be  $2.8 \times 10^{-14}$   $\text{cm}^2$ . Similarly, for Ar and He the broadening coefficients of 0.73 and 1.3 G/torr were obtained, respectively. It is interesting to compare available cross sections for  $P$ -state atoms. Table I gives the data obtained in this work as well as those measured by Westenberg and deHaas.<sup>1</sup> The value for Cl broadened by  $\text{Cl}_2$  was recalculated from the data given by Beltran-Lopez and Robinson<sup>5</sup> assuming the broadening was primarily a function of the  $\text{Cl}_2$  pressure. Similarly, the cross section for the  $^3P_2$  lines of O broadened by  $\text{O}_2$  were recalculated from the data of Radford and Hughes.<sup>6</sup>

For all the atoms listed, the cross sections are generally larger than the geometrical cross sections determined from transport properties. This appears to be generally true for non- $S$ -state atoms, where coupling between orbital or rotational and spin angular momenta can occur.

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### <sup>13</sup>C Chemical Shielding Anisotropy in Solids. $\text{CS}_2$ and $\text{CaCO}_3$ \*

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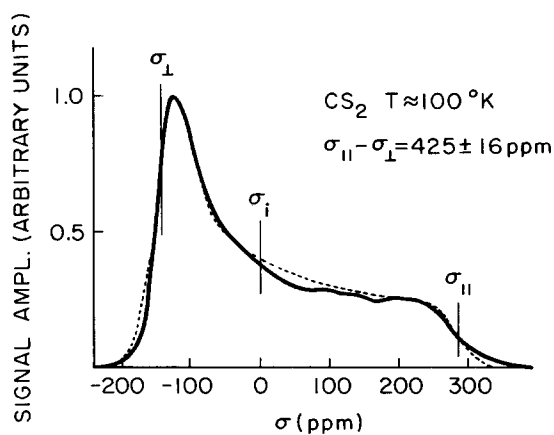
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An area of nuclear magnetic resonance which has aroused considerable interest in recent years is the study of chemical shielding anisotropies ( $\Delta\sigma$ ).<sup>1</sup> The loss of information about the chemical shielding tensor ( $\sigma$ ) due to motional averaging in liquids has been partially overcome through the use of liquid crystal solvents.<sup>1a</sup> It is known, however, that studies in the solid state offer

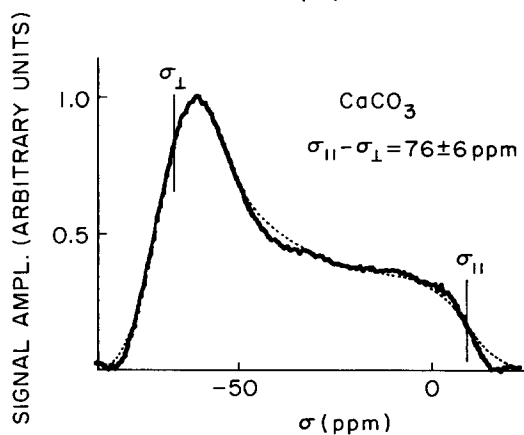
the advantage of obtaining fuller information about  $\sigma$  when the problems of dipolar broadening can be coped with. In <sup>13</sup>C spectroscopy, where dipolar coupling among the <sup>13</sup>C spins is very small, making the application of complicated coherent-averaging techniques<sup>2</sup> extraneous, the signals are extremely weak and information about  $\sigma$  has been obtained only in rare

cases.<sup>3</sup> As an example of a favorable case where an isotopically enriched  $^{13}\text{C}$  sample can be put to good use, we have studied solid  $\text{CS}_2$  (60 atom%  $^{13}\text{C}$ ) at  $\approx 100^\circ\text{K}$ . This measurement is of particular interest since McConnell and Holm have invoked nuclear spin relaxation via  $\Delta\sigma$  to explain the unusually short  $T_1$  in liquid  $\text{CS}_2$ .<sup>4,5</sup> This was strengthened in an experiment where  $(T_1/T_2)$  was found to be  $\approx 7/6$ .<sup>6</sup> More recently, a careful study of the temperature and field dependence of  $T_1$  has shown that both  $\Delta\sigma$  and spin-rotation interaction contribute to  $T_1$  as expected<sup>7</sup>; a value for  $\Delta\sigma$  of  $438 \pm 44$  ppm has been calculated from these measurements.<sup>8</sup>

In Fig. 1(a) we see a digitally smoothed Fourier-transform spectrum of solid  $\text{CS}_2$ . The sample was equilibrated at room temperature in the magnetic field



(a)



(b)

FIG. 1. (a) Absorption spectrum of solid  $\text{CS}_2$  (60 atom%  $^{13}\text{C}$ ) obtained from Fourier transformation of the free induction signal at  $\approx 100^\circ\text{K}$ . The solid line is a digitally smoothed experimental accumulation of three such signals and the dotted line a computer generated powder pattern used to extract the shielding parameters. (b) Fourier transform of response to a modified DEFT sequence in powdered  $\text{CaCO}_3$  (nat. abund.  $^{13}\text{C}$ ). Recycle time was 64 sec and accumulation time 10 h.

(utilizing the short  $T_1$  of  $\approx 40$  sec)<sup>6</sup> and the spectrum taken at 14.4 MHz after cooling to  $100^\circ\text{K}$  where molecular reorientation is expected to be severely inhibited. The curve is a characteristic axial symmetry powder pattern<sup>9</sup> and the elements of  $\sigma$  as determined by fitting the experimental spectrum with a computer generated powder pattern are:  $\sigma_{33} = \sigma_{11} = 285 \pm 10$ ,  $\sigma_{11} = \sigma_{22} = \sigma_{\perp} = -140 \pm 6$  ppm, referred to the room temperature isotropic chemical shift ( $\sigma_i$ ). The anisotropy  $\Delta\sigma = \sigma_{11} - \sigma_{\perp} = 425$  ppm which corroborates remarkably well the prediction of Spiess *et al.*<sup>8</sup> The natural dipolar linewidth was observed to be about 600 mOe.

In other cases, where favorable enriched samples with large anisotropies, or single crystals are not available, the extraction of  $^{13}\text{C}$  nuclear signals in solids (where  $T_1$  is characteristically extremely long) presents a more formidable task. We have found that the application of some recently developed high sensitivity spin-echo techniques<sup>10-12</sup> is particularly well suited to this kind of problem, and we report on a preliminary example of such an experiment performed on powdered  $\text{CaCO}_3$ . Figure 1(b) shows the signal obtained from Fourier transformation and digital smoothing of the response of the above sample to a modified DEFT sequence.<sup>13</sup> Under the same conditions we found that a normal single pulse Fourier-transform experiment yields practically nothing. The principal values of  $\sigma$  using  $\text{C}_6\text{H}_6$  as a reference are:  $\sigma_{11} = 10 \pm 3$ ,  $\sigma_{\perp} = -66 \pm 3$  ppm, yielding  $\Delta\sigma = 76$  ppm in good agreement with the precise value of 75 ppm determined by Lauterbur.<sup>3</sup> In cases where other nuclei with magnetic moments create a problem, their effects can be removed by multiple-resonance techniques.<sup>14</sup>

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## Intermolecular Potential in Liquid Argon

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Analysis of the equation of state for gases<sup>1</sup> shows that there is a linear relation between the experimental temperatures and densities ( $\tilde{T}$ ,  $\tilde{\rho}$ ) at which the compressibility factor  $c \equiv \beta p / \rho$  equals unity:

$$\tilde{T} = a - b\tilde{\rho}. \quad (1)$$

The critical compressibility factor for a fluid is less than unity which suggests that relation (1) may also be valid for liquid densities. However, new experimental data for liquid argon<sup>2,3</sup> show a small but systematic deviation from Eq. (1) [ $(\tilde{T}_{\text{exp}} - \tilde{T}_{(1)}) / \tilde{T}_{(1)} \lesssim 1\%$ ] proving that Eq. (1) is not strictly valid for liquid argon.

The (approximate) validity of Eq. (1) for both the low density gas and the liquid indicates that a liquid may be described with the same potential function that can be used to obtain the equation of state for a dilute gas. From the virial expansion one obtains<sup>4</sup>  $a = T_B$  and  $b = C(T_B) / B'(T_B)$ , where  $T_B$  is the Boyle temperature and  $B$  and  $C$  are, respectively, the second and third virial coefficient ( $B' \equiv dB/dT$ ). As the constant  $b$  depends on the (unknown) nonadditive three-body potential, the linear relation (1) is determined by the same two- and three-body potential function which reproduces  $B$  and  $C$ . Nevertheless, liquid PVT properties calculated by the molecular dynamics (MD) technique<sup>5</sup> using a Lennard-Jones 12-6 pair potential are in excellent agreement with the experimentally obtained values for argon, reduced with the values of the potential parameters determined only from an analysis of  $B(T)$ . This shows that it is possible to describe both a dilute gas and a liquid by the same effective pair interaction function. Furthermore, the agreement between MD calculated and experimentally obtained values of  $p(\rho, T)$  implies that a Lennard-Jones 12-6 fluid obeys Eq. (1) to the same extent as does liquid argon.

To determine whether the linear relation (1) between  $\tilde{T}$  and  $\tilde{\rho}$  is specific for a Lennard-Jones 12-6 fluid, we

calculated points of state ( $\tilde{T}^*$ ,  $\tilde{\rho}^*$ ) using the Barker-Henderson fluid model<sup>6</sup> and a Lennard-Jones  $n-6$  pair-interaction function with  $n=9, 12$ , and 18. In all three cases,  $\tilde{T}$  and  $\tilde{\rho}$  were nearly linearly related; however, the slope of the straight line was extremely sensitive to the shape of the potential.<sup>7</sup> The calculated points of state were compared with the corresponding experimental values by reducing  $(\tilde{T}, \tilde{\rho})_{\text{exp}}$  with parameter

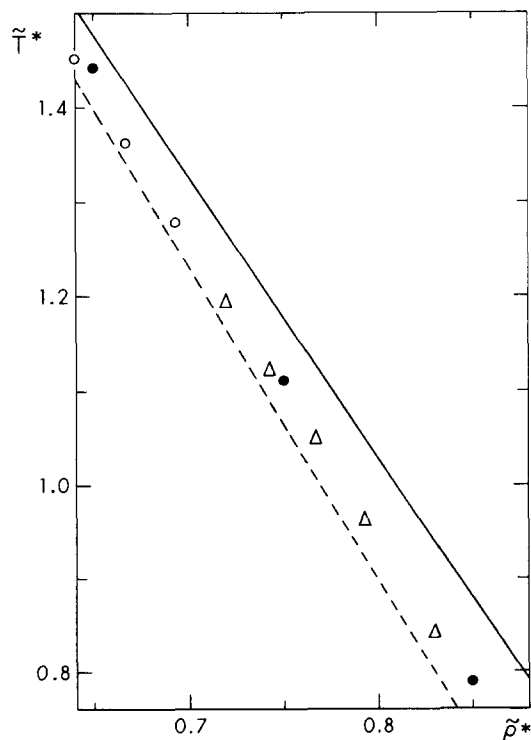


FIG. 1.  $\tilde{T}^*(\tilde{\rho}^*)$  for a Lennard-Jones 12-6 fluid. The points marked  $\Delta$  and  $\circ$  are calculated from experimental values of  $p(T, \rho)$  taken from Refs. 2 and 8, respectively. The points marked  $\bullet$  are determined from Molecular Dynamic results taken from Refs. 5 and 10. The full line shows Eq. (1). The dotted line gives the corresponding values using the liquid model from Ref. 6.