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Abstract: We have measured the proton ioiigitudinal spin relaxation rate in dilute gaseous silane (SiH$_4$ between 10^{-2} and I amagats and are able to observe the influence of rotational Q branch centrifugal distortion transitions.

In order to interpret nuclear spin relaxation measurements in dilute methane (CH$_4$) gas, the effects of Q branch rotational centrifugal distortion transitions had to be taken into account. This was first done phenomenologically (Beckmann et al. (1972), henceforth referred to as BBB) and, subsequently, in terms of a detailed relaxation theory in which the rotational structure of the methane molecule was explicitly taken into account (Beckmann et al. (1976), henceforth referred to as BBO). In this paper we wish to report measurements of the longitudinal relaxation rate T_1^{-1} as a function of density in dilute silane (SiH4) gas at room temperature. The results are shown in Fig. 1 and the reader is referred to BBB and BBO for a discussion of the nuclear magnetic resonance background, the details of the experimental apparatus and technique, and the role of centrifugal distortion. The major drawback to the measurements in Fig. 1 is that we have not gone to sufficiently low density to properly characterize the T_1^{-1} maximum. Since these measurements were performed, however, the rotational structure of the silane molecule has been investigated in detail by Ozier et al (1976), and we feel it important to note that this structure manifests itself in the relaxation experiments.

The expression for T_1^{-1} which incorporates the effects of centrifugal distortion in a phenomenological way is given by BBB (see BBO also),

$$[1] \quad T_1^{-1} = \frac{2\pi^2 kT}{B_0 hc} \left\{ C_a^2 \frac{2\tau}{1 + \omega_0^2 \tau^2} \right. $$
$$ \left. + b C_d^2 \frac{2\tau}{1 + \Omega^2 \tau^2} \right\} $$

where B_0 is the rotation constant (Ozier et al. 1976) and C_a and C_b are the scalar and tensor spin rotation coupling constants (Ozier et al. 1968). The nuclear Larmor frequency is $\omega_0/2\pi = 30$ MHz and $\Omega/2\pi$ is an 'average' centrifugal distortion frequency (BBB). The correlation time τ for molecular reorientation is related to the density ρ by $\tau^{-1} = \langle\sigma\upsilon\rangle\rho$ (BBO). The parameter b can be taken to be 4/45 (BBO).

At the density where $\tau^{-1} = \tau_{MAX}^{-1} = \omega_0$, the second term in [1] can be neglected if $\omega_0 \ll \Omega$. Under these conditions, $(T_1^{-1})_{MAX}$ can be calculated with no adjustable parameters since B_0 and C_a are well known. This value is $(T_1^{-1})_{MAX} = 115$ s^{-1} and agrees very well with the experimental value in the vicinity of 0.02 amagats. At high densities where $\omega_0^2\tau^2$ and $\Omega^2\tau^2 \ll 1$, $(T_1\tau)^{-1}$ is constant (i.e., $T_1^{-1}\rho$ is constant) and the value of $\langle\sigma\upsilon\rangle = 1.1 \times 10^{10}$ (amagats s)$^{-1}$ is obtained from the measurements using the known values of B_0, C_a, and C_d. In turn, the procedure for determining an effective cross section for molecular reorientation can be found in BBO. The contribution to the C_a term is, then, completely specified and is shown in curve {a}

in Fig. 1. The only remaining parameter is Ω and $\Omega/2\pi = 200$ MHz was used to generate curve (*b*) in Fig. 1. Curve (c) is (*a*) plus (*b*). The fact that C_d is only known to $\pm40\%$ (Ozier et al. 1968) coupled with the incompleteness, of the present results means that the values $\langle\sigma\upsilon\rangle$ and Ω are only known to about $\pm25\%$. It is interesting to compare the value obtained for Ω. with that used to fit the methane experiments ($150 < \Omega/2\pi < 240$ MHz) (BBB). The relaxation experiments are clearly not sensitive enough to determine if Ω is different for the two gases. The important feature, and indeed, the purpose of this paper, is to show that $\Omega \gg \omega_0$: i.e., the centrifugal distortion transitions must be taken into account in interpreting the nuclear spin relaxation experiments. The phenomenological treatment of the problem given here is the same as that which has been used in methane (BBB); the detailed theoretical treatment of centrifugal distortion effects in methane (BBO) could now be applied to silane since the rotational structure is now known (Ozier et al. 1976). We note that at lower temperatures, the concept of an average distortion frequency becomes meaningless since individual transitions in low-lying rotational *J* states become important (BBO). The same is true when the nuclear Larmor frequency is coincident with a distortion frequency (BBO). In fact, it may be that the proposals for doing 'relaxation rate spectroscopy' in methane (BBB, BBO) might be better suited to silane since there are several important distortion transitions in the tens of megahertz region (Ozier et at. 1976). We note that to measure T_1 at densities lower than those reported here is difficult, but well within present technology (BBO).

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BECKMANN.P. A., BLOOM, M., and OZIER, I. 1976. Can. J. Phys.54, 1712.
OZIER, I., CRAPO, L. M., and LEE, S. S. 1968. Phys. Rev. 172,63.
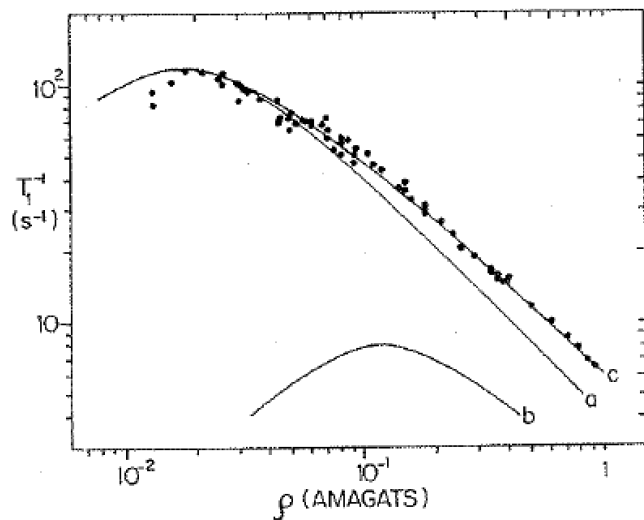OZIER, I., LEES, R. M., and GERRY, M. C. L. 1976. Can. J, Phys.54, 1094.

Figures:

Fig. 1. The proton longitudinal relaxation rate T_1^{-1} in gaseous SiH_4 at room temperature as a function of density. Curves (a) and (b) represent the C_a and C_d terms in [1] and (c) is their sum. The parameters are given and discussed in the text.