Rev. Sci. Instr. 37, 1655 (1966).

[4] W. Aberth and J. R. Peterson, Rev. Sci. Instr. 38, 745 (1967).

[5] H. C. Hayden and N. G. Utterback, Phys. Rev. 135, A1575 (1964); E. S. Chambers, Phys. Rev. 133, A1202 (1964); V. G. Tel'kovskii, Dokl. Akad. Nauk SSSR 108, 444 (1956) [translation: Soviet Phys.—Dokl. 1, 334 (1956)].

[6] D. R. Bates and J. T. Lewis, Proc. Phys. Soc. (London), Ser. A 68, 174 (1954).

NUCLEAR SPIN RELAXATION IN POLYATOMIC GASES: A NEW EFFECT*

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We have observed a very striking density dependence of the proton spin-lattice relaxation time T_1 in gaseous fluoroform (CHF_3) and methyl fluoride (CH_3F). Although a complete interpretation is not possible at this time, measurements of the type which we report here should be very useful in the determination of anisotropic intermolecular potentials for symmetric-top molecules.

Background.—Nuclei of spin $\frac{1}{2}$ are coupled to the molecular rotation by the intramolecular spin-rotation and dipolar interactions. For a dilute gas, the interactions between nuclei on different molecules may be neglected. Molecular collisions cause transitions between the rotational states of the individual molecules which result in a modulation of the intramolecular interactions. This enables the nuclear Zeeman system to exchange energy with the system of rotational and translational degrees of freedom of the molecules. For dilute gases, a relationship has been derived[1] between T_1, the coupling constants of the spin-rotation and dipolar interactions, and their correlation times τ_1 and τ_2, respectively. Since τ_1 and τ_2 are normally inversely proportional to the density ρ for dilute gases, and since it is difficult to observe the NMR signal at sufficiently low densities to violate the condition $\omega_0\tau_1, \omega_0\tau_2 \ll 1$, one usually observes a linear dependence of T_1 on density[1-3]:

$$T_1 = A\rho, \tag{1}$$

where A is a function of temperature only.

Observations.—We have measured T_1 as a function of density and temperature for the fluorine and proton spins in CHF_3 and CH_3F. The results for CHF_3 are presented in Fig. 1 in the form of a plot of T_1/ρ as a function of ρ at several temperatures. Similar results were obtained for CH_3F. If Eq. (1) holds, this plot gives a horizontal line. The new effect we report here is that, whereas Eq. (1) correctly describes the relaxation of the fluorine spins, the dependence of T_1 on ρ for the protons is quite different. For the protons, the curves of T_1/ρ vs ρ appear to have "steps" as indicated by the solid lines drawn through the data. These solid lines have no theoretical significance, however, and we have indicated, by the dashed line drawn through the room-temperature points in Fig. 1, an alternative curve which fits the data as well as the solid lines. Our room-temperature results are in agreement with those previously reported[4] for CHF_3 provided that the proton T_1 measurements of Johnson, Waugh, and Pinkerton[4] were carried out at densities less than 20 amagat where our first break occurs. As these authors point out, the fluorine spin relaxation is dominated by spin-rotation interactions while dipolar interactions may contribute appreciably to the proton relaxation rate. To complete the description of our experimental observations, we are able to fit the temperature dependence of the coefficient A in Eq. (1) for the fluorine T_1/ρ very well by $A \propto T^{-n}$, where $n = 2.5 \pm 0.1$ for CHF_3 and $n = 1.63 \pm 0.05$ for CH_3F. A similar behavior is found for CF_4 where $n = 1.65 \pm 0.1$. The fluorine T_1/ρ for CF_4 and CH_3F at room temperature were found to be 2.1 ± 0.05 msec/amagat and 44 ± 1 msec/amagat, respectively.

Sample purity.—The samples of CHF_3 and CH_3F gases were obtained from Matheson of Canada, Ltd., who specified the minimum purity to be 98 and 99%, respectively. By means of a mass-spectrometer analysis, we have shown that the O_2 concentrations in CHF_3 and CH_3F are less than 0.01 and 0.1%, respectively. We have also measured the proton T_1 in a sample of CHF_3 containing 0.35% of oxygen and have obtained results very similar to those previously reported[5] for C_2H_4 with oxygen added. This indicates that the novel features of the data presented in Fig. 1

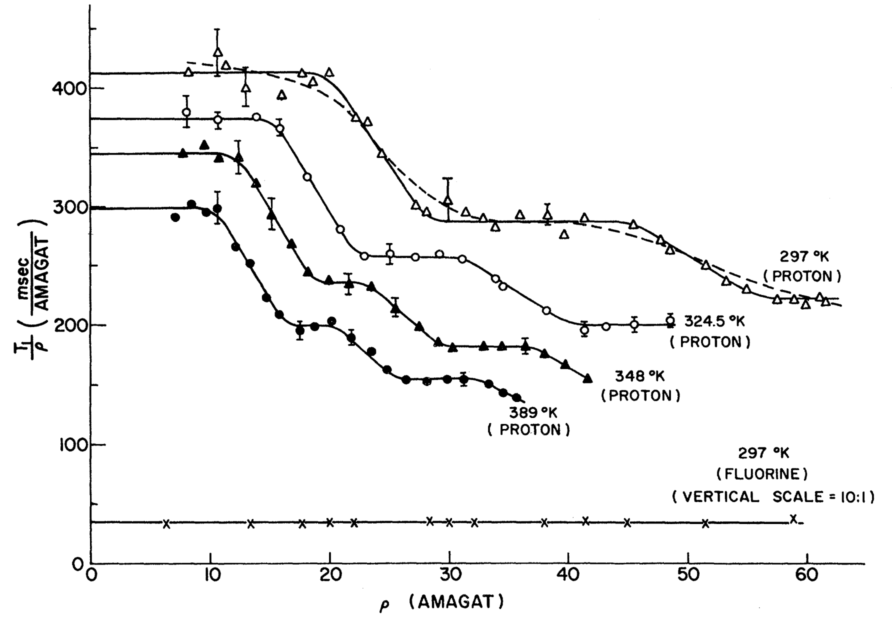

FIG. 1. Plot of T_1/ρ vs ρ for protons and fluorine nuclei in CHF_3 gas. The densities are expressed in ideal amagats, one such unit corresponding to 2.69×10^{19} molecules/cm^3. The dependence of ρ on temperature and pressure was supplied to us by General Chemical Division, Allied Chemical Co. These values were confirmed to within a few percent error by measurements of the proton magnetic resonance signal strength. The value of T_1/ρ for the fluorine spins is 3.5 msec/amagat.

are not due to paramagnetic impurities.

Interpretation.—We suggest that the peculiar dependence of the proton T_1/ρ on ρ is due to the fact that the intramolecular dipolar interactions make an appreciable contribution to the proton relaxation rate. It has been pointed out previously[1] that in a very dilute gas only a small fraction of the dipolar interaction is effective in producing spin relaxation. This is so because the dipolar interaction transforms under rotations as the spherical harmonic $Y_{2m}(\Omega)$ and has matrix elements connecting states having differences in the rotational quantum numbers $\Delta J = 0, \pm1, \pm2$; $\Delta K = 0, \pm1, \pm2$. At low densities where the rotational levels are sharp, the high-frequency dipolar terms arising from rotational states of different energy must be dropped insofar as nuclear spin relaxation is concerned. This reduces the contribution of the dipolar interactions to the spin relaxation rate in spherical-top molecules by a factor of exactly 5. This reduction factor in symmetric top molecules can be much greater.[1,6] We believe that the breaks in the dependence of T_1/ρ on ρ arise when groups of rotational levels are collision broadened by an amount of order of the characteristic frequencies of the oscillating terms in the dipolar interactions. Such effects have already been discussed with respect to nonresonant absorption measurements.[7-9] In order to analyze our results, more accurate measurements of the spin-rotation coupling constants for CHF_3 and CH_3F are required.[10] The spin-rotation interaction has negligible high-frequency matrix elements, thus accounting in our picture for the constancy of T_1/ρ of the fluorine spins. With the availability of the spin-rotation coupling constants, the proton dipolar contribution could be obtained from the experimental values of T_1 for proton and fluorine spins. Even then more experimental information is required to test the influence of nuclear spin symmetry, molecular symmetry, and intermolecular interactions on the observed effects. To clarify these points we are carrying out further experiments on mixtures of CHF_3 and CH_3F with other gases and on the deuterated molecules. We are also planning to perform double resonance experiments such as those previously performed on liquid CHF_3.[11]

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[1] M. Bloom, F. Bridges, and W. N. Hardy, Can. J. Phys. 45, 3533 (1967).

[2] The characteristic T_1 minimum at lower densities has been observed only for H_2 [W. N. Hardy, Can. J. Phys. 44, 256 (1966)], for HD [R. G. Dorothy, thesis, University of British Columbia, 1967 (unpublished)], and for CH_4 [M. Bloom and R. G. Dorothy, Can. J. Phys. 45, 3411 (1967)].

[3] For a survey of systems in which this linear dependence of T_1 on ρ has been observed, see Ref. 1 and the review article by M. Bloom and I. Oppenheim, Advan. Chem. Phys. 12, 549 (1967).

[4] C. S. Johnson, Jr., J. S. Waugh, and J. N. Pinkerton, J. Chem. Phys. 35, 1128 (1961).

[5] M. Bloom, M. Lipsicas, and B. H. Muller, Can. J. Phys. 39, 1093 (1961).

[6] These effects probably play an important role in some liquids composed of "nearly spherical" molecules; cf. M. Bloom, Proceedings of the International Conference on Magnetic Resonance and Relaxation, Fourteenth Colloque Ampère, Ljubljana, Yugoslavia, September, 1966, edited by R. Blinc (North-Holland Publishing Company, Amsterdam, The Netherlands, 1968), pp. 202-214.

[7] G. Birnbaum, Phys. Rev. 150, 101 (1966); G. Birnbaum and A. A. Maryott, J. Chem. Phys. 21, 1774 (1953), and 32, 686 (1960).

[8] A. Ben-Reuven, Phys. Rev. 145, 7 (1966).

[9] R. G. Gordon, J. Chem. Phys. 46, 448 (1967).

[10] We have been informed privately by Dr. I. Ozier that these data will soon be available from molecular beam measurements performed in the laboratory of Professor N. F. Ramsey at Harvard University.

[11] J. H. Chaffin, III, and P. S. Hubbard, J. Chem. Phys. 46, 1511 (1967).

DIRECT OBSERVATION OF METHYL LIBRATIONS IN NEOPENTANE*

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The "small-κ" method of neutron molecular spectroscopy has been used to observe for the first time the two librational modes, A_2 and F_2, of the methyl groups in neopentane. Two inelastic-scattering peaks corresponding to librational modes were measured at 26 and 33 meV, the separation resulting primarily from a difference in the sixfold energy barriers governing the two rotations. Both librational motions were restricted by a dominant threefold energy barrier of +870 ± 30 MeV.

Of the 19 vibrational frequencies expected in neopentane, $C(CH_3)_4$, five are associated with symmetries which are infrared and Raman inactive,[1,2] and therefore cannot be studied directly by these means. Rush[3] recently exhibited that the methyl librational motions which are numbered among the optically inactive frequencies could be observed in a single broad band with cold neutrons inelastically scattered from the methyl protons in neopentane. We wish to report for the first time the resolution of this broad band into two separate peaks corresponding to the two anticipated librations of symmetry A_2 and F_2. The peak intensities were found to reflect the onefold and threefold degeneracies associated with the symmetries of these two librational modes provided that the Boltzmann correction is made in the populations of the different levels and that differences in the proton displacements in the two modes are considered. Since the potential wells governing the librational motions of the CH_3 groups appear to be sufficiently deep, considerations which are needed to deal with tunneling between different CH_3 conformations[4,5] were omitted.

The relatively high resolution achieved in this scattering experiment results from utilizing the smallest possible scattering angles and incident neutrons with higher than customary energy. This experimental arrangement, which is called the "small-κ" method, minimizes the momentum exchanges between the sample and thermal neutrons. As the widths of both elastic and inelastic peaks in the neutron spectra of a gas sample are