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Observation of spin conversion in solid $^{13}CH_3D$ by NMR†

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The temperature dependence of the proton magnetic susceptibility in $^{13}CH_3D$ has been measured throughout the temperature range from 1.6 to 95 K by cw NMR techniques. The observations were calibrated by an internal ^{13}C spin thermometer. At 1.8 ± 0.3 K the mean-squared angular momentum of the protons $\langle I(I+1)\rangle$ was 2.71 ± 0.07. This value was significantly larger than the classical value of 2.250, due to nuclear spin conversion. At 11.4 K the conversion time constant was estimated to be ~ 30 h.

Methane and its deuterated forms exist as molecular crystals at low temperatures. Many of the properties of the methanes can be understood by analogy with those of the solid hydrogens, as discussed in a recent review.[1] Until now, the observation of spin conversion at 4 K has been limited to H_2, D_2 and CH_4. Of the deuterated methanes, CH_3D is the one most likely to exhibit spin conversion. The nuclear spin-wave functions of CH_3D must be invariant under rotations of $\frac{2}{3}\pi$ about the C–D bond, since all three protons are equivalent. This requirement results in four of the eight spin-wave functions belonging to a one-dimensional representation (A) with $I=\frac{3}{2}$ and the remaining four belonging to two two-dimensional representations (E) with $I=\frac{1}{2}$.[2]

The wave function ψ contains a sum over terms of the form $\phi_\zeta(J,K)\chi_\xi(I)$, where $\phi_\zeta(J,K)$ is a linear combination of rotational (or orientational) wave functions for a symmetric top, J is the angular momentum, and K is the projection of the angular momentum along the direction defined by the C–D bond, $\chi_\xi(I)$ is a linear combination of spin-wave functions with spin I, and ζ and ξ are symmetry labels. The total wave function has to be of A-type symmetry in order for Fermi-Dirac statistics to be obeyed. As a result, only certain combinations of the $\phi_\zeta(J,K)$ and $\chi_\xi(I)$ are allowed.

Using a quantum-mechanical extension of the James-Keenan model,[3] based on the octopole-octopole intermolecular interaction, an approximate energy-level scheme has been calculated by Yamamoto and his co-workers. Ignoring the effect of spin conversion and limiting the calculations to the subspace $J \leq 4$, the energy levels contained in Fig. 1 have been obtained.[4] The average value of $I(I+1)$ can be calculated from the expression

$$\langle I(I+1)\rangle = \tfrac{15}{4}\, p_A + \tfrac{3}{4}\, p_E\,, \qquad (1)$$

where p_A and p_E are the respective probabilities of the A and E levels being occupied, as given by Boltzmann statistics and where $\frac{15}{4}$ and $\frac{3}{4}$ are the values of $I(I+1)$ for the A and E states, respectively.

Calorimetric measurements[5-7] have indicated that p_A probably increases beyond its high-temperature value of $\frac{1}{2}$ for $T \lesssim 2$ K. However, no previous experiment has conclusively demonstrated such a change in p_A. It is this change in spin isomer concentration which is called spin conversion. In the present experiment, $\langle I(I+1)\rangle$ for the protons was measured by a direct comparison with $\langle I(I+1)\rangle$ for ^{13}C. Since the integrated signal intensity S in a cw NMR experiment is proportional to the magnetization, the value of $\langle I(I+1)\rangle$ can be determined from the relationship[8]

$$\langle I(I+1)\rangle = q\left(\tfrac{3}{4}\right)\left(\gamma_C S_p / \gamma_p S_C\right)\,, \qquad (2)$$

where q is the fraction of CH_3D molecules having the ^{13}C isotope, γ_C is the gyromagnetic ratio for ^{13}C and γ_p is the gyromagnetic moment for ^1H.

The NMR spectrometer employed a Q-meter

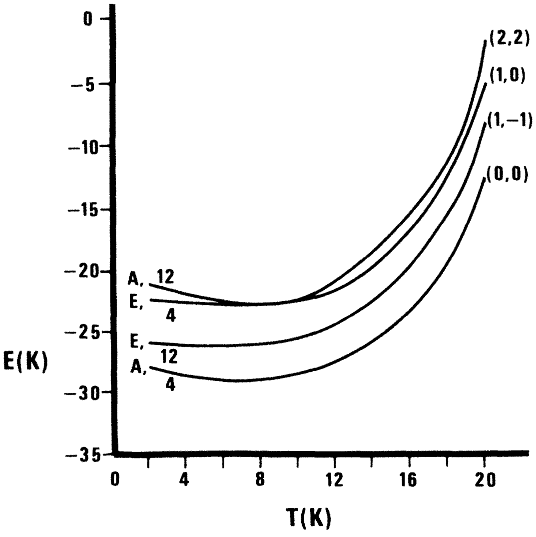

FIG. 1. Energy-level scheme for CH_3D (Ref. 4). The number attached to the left of each level shows its total degeneracy. The numbers to the right of each level are the quantum numbers (J,K).

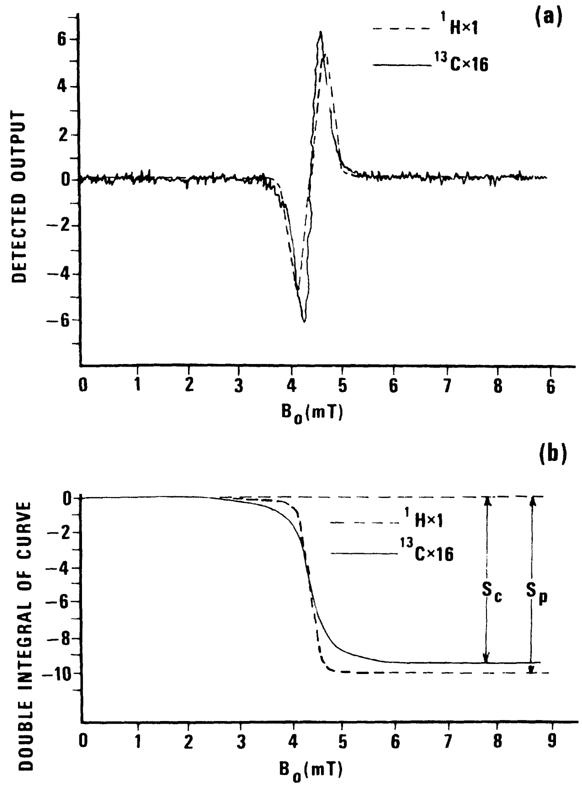

FIG. 2. Typical measurement of S_p/S_C at 1.77 K. The curves for the ^{1}H nuclei are the average of 8 scans, each of 30 sec. The curves of the ^{13}C nuclei are the average of 64 scans, each of 30 sec.

detector as previously described[9,10] operating at 9.3 MHz. The sample was supplied by Merc Sharp and Dohme of Canada to a specification of 98% deuteration and 80% ^{13}C labeling. T_1 was found to be ~0.1 sec at ~100 K. This corresponds to an oxygen concentration of ~0.4%,[11] which should help increase the spin conversion rate. The ratio S_C/S_p was measured to be 0.065 in the liquid. This is equivalent to a value for q of 0.775 which is slightly less than the manufacturer's estimate of 0.80. As a result the accuracy of measuring this ratio was determined by the signal-to-noise ratio on the ^{13}C signal. To obtain the best accuracy possible, the peak-to-peak modulation of the magnetic field was set equal to the ^{13}C linewidth at each temperature. By performing a Fourier expansion of the output of the phase-sensitive detector,[12] it is easy to show that

$$S \propto M_0 B_m\,, \tag{3}$$

where M_0 is the static magnetization and B_m is the modulation amplitude of the modulating magnetic field. This result is true even at large modulation amplitudes provided that the magnetic sweep width used is large enough to observe the entire line. Hence we obtain the exact relationship

$$S_p/S_C = M_{0p}/M_{0C}\,. \tag{4}$$

The magnitude of the rf magnetic field was kept less than 0.5 μT in order to avoid saturation that would invalidate Eq. (2). The only relevant error in $\langle I(I+1)\rangle$ is a result of the statistical error in the ratio S_p/S_C, due mainly to the low-frequency noise in the spectrometer. A typical measurement of S_p/S_C at 1.77 K is shown in Fig. 2. The ^{1}H and ^{13}C nuclei were measured with the same settings of the spectrometer. In order to accurately digitize both the ^{1}H and ^{13}C signals the gain switch on the analog to digital converter was changed by a factor of 8. The linearity of this gain control was found to be better than 0.25% and therefore did not give rise to a significant systematic error.

Temperature regulation of the sample was achieved by using a Lakeshore Cryotronics capacitance controller model CSC 400. Maximum variation in the temperature was less than 0.5% over the entire temperature range. The temperature was measured with a calibrated Lakeshore Cryotronics carbon-glass resistance thermometer. The manufacturer's calibration of the thermometer was checked at 4.2 K and was found to be accurate to within 0.25%. At 77.4 K it was accurate to within 0.5%. The ^{13}CH$_3$D sample was slowly cooled and the solid formed over several hours. The sample was carefully annealed for at least one hour each time it passed through a phase transition. Because recent neutron total cross-section measurements[13] indicated that equilibrium of the spin isomers in phase III takes about three days, in one experiment the sample was kept at ~11.4 K for three days before proceeding to lower tem-

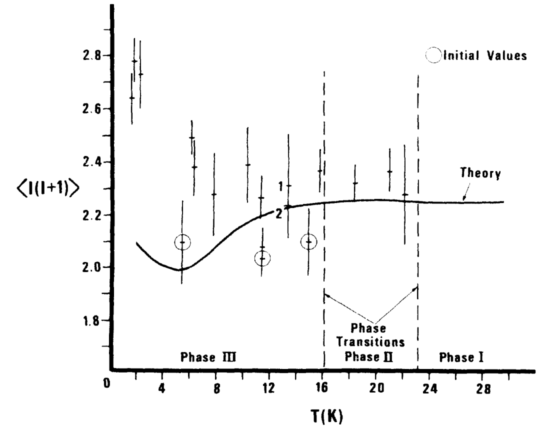

FIG. 3. $\langle I(I+I)\rangle$ as a function of temperature T for ^{13}CH$_3$D. The solid line was calculated from the energy-level scheme in Fig. 1. The method of establishing the error bars for each point is given in the text.

peratures. As shown in Fig. 3, the value of $\langle I(I+1)\rangle$ increased with time. The initial values, indicated by open circles, were obtained from measurements made less than 12 h after establishing the desired temperature. At 11.4 K it reached its final value in ~30 h. Point 1 was measured ~2 h after the sample was at 6.1 K and point 2 was measured ~7 h later. Due to the errors involved, it was not possible to observe hysteresis at this temperature. Hysteresis was expected from the recent neutron total cross section measurements.[13] At each temperature the ratio S_p/S_C was measured many times over a period of many hours, the temperature being held constant to within 0.5%. The data was stored on magnetic tape and doubly integrated on a Nicolet Instrument Corporation Model 1072 instrument computer.

Using the same sample of $^{13}CH_3D$, the value of $\langle I(I+1)\rangle$ was also determined by using the ^{19}F in the Teflon coil form as the reference. The measured curve had the same shape as in Fig. 3 but with slightly lower values. This was probably due to the ^{13}C being ~0.3 K warmer than the ^{19}F due to a heat leak down the glass sample tube.

The values shown in Fig. 3 were obtained by taking $\langle I(I+1)\rangle = \frac{15}{4}$ in the liquid. The ratio S_p/S_C for the liquid was measured for over two days, resulting in an error of ±2.0%. The errors indicated in Fig. 3 were obtained by adding the error S_p/S_C for the liquid to that in S_p/S_C for the temperature being considered. When one more than one measurement was made at a particular temperature, the mean was obtained by weighting the individual results by their $1/\sigma$ values. Results similar to those shown in Fig. 3 were also obtained from a pure sample $^{12}CH_3D$ used by Morrison, and kindly supplied by him.

The present results are substantially in agreement with a previous determination of $\langle I(I+1)\rangle$ by cw NMR.[14] However the present improved experiment eliminated several systematic errors in the measurement of the proton temperatures, and has definitely established the presence of spin conversion in solid CH_3D for the first time. The poor agreement between the present results and that calculated from the published energy levels is most likely due to ignoring the effect of spin conversion when calculating the energy levels. This is plausible since in the case of CH_4, only when spin conversion was taken into account[15] were the calculated results in good agreement with experiment.

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