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Spin-species conversion rate in solid CH_4 in the temperature range 4–23 K

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By monitoring the time dependence of the nuclear magnetic susceptibility we have measured the spin-species conversion rate in solid CH_4 for temperatures of 4–23 K. We discuss the relation to previous measurements and to the available theory of spin-species conversion.

Methane molecules in their ground electronic and vibrational state may be classified into three distinct spin species, according to the representation of the tetrahedral group (A, F, or E) to which their orientational wave functions belong. Because of the exclusion principle for protons, each spin species is associated with a unique value of the total nuclear-spin quantum number I: A with $I=2$, F with $I=1$, and E with $I=0$. Conversion between spin species is inhibited because it involves a simultaneous nuclear and orientational transition.

The conversion rate in the solid has been measured using NMR for temperatures up to 6 K.[1–4] In this Brief Report we present an extension of these measurements to 23 K. Lushington and Morrison[5] have measured the conversion rate by observing changes in the total scattering cross section for neutrons, in the temperature range 7–16 K. However, the neutron counting rate limited the statistical accuracy of their measurements at the higher temperatures, where the conversion rate becomes rapid.

Solid methane exhibits a phase transition to an eight-sublattice orientationally ordered state at 20.4 K. This transition is remarkable in that the rotations of the molecules on six of the sublattices are strongly hindered by the collective molecular field, while the molecules on the other two sublattices remain essentially free rotors.[6] Measurements of the proton magnetic susceptibility by Code and Higinbotham[7] suggested that spin-species conversion was much faster for the free-rotor molecules than for the rotationally hindered molecules.

A calculation by Nijman and Berlinsky[8] supports this picture. They show that the dominant conversion processes at low temperature all involve the spontaneous emission of a single phonon to conserve energy. The interspecies energy differences for the free-rotor molecules are about 15 K, as they are for a free molecule. The rotationally hindered molecules, on the other hand, have much smaller energy differences, arising from the small matrix element for a molecule to tunnel between equivalent minima in the orientational potential.[9] The smaller conversion rate for the rotationally hindered molecules results from the relative inefficiency of phonon emission at the lower energy, and from the small matrix elements of the dominant conversion process between rotationally hindered states.[8]

As in the earlier measurements by other workers,[1–4] the conversion rate was measured by monitoring the relaxation of the nuclear susceptibility to its equilibrium value after a sudden change in temperature. This susceptibility is proportional to $\langle I(I+1)\rangle$, which, in turn, depends upon the relative populations of the three spin species. In practice, the area of the NMR absorption line at a Larmor frequency of 280 MHz is measured at 3-min intervals by numerically integrating a digitized derivative line. A relative accuracy of about 1% is achieved. Our procedure for measuring NMR line areas has been described previously.[10] The samples used were "research grade" methane with a quoted oxygen content of 2 ppm.[11] This is much less than the level found to increase the spin conversion rate at low temperature (170 ppm).[2] The samples were condensed and solidified over a period of about 2 h, then rapidly cooled to liquid-helium temperature. This corresponds roughly to the "slow" condensation procedure of Ref. 2.

For temperatures below about 10 K, the conversion rate was measured by rapidly cooling the sample from about 25 K to the desired temperature. However, for temperatures of 8 K and above, a better ratio of initial to final areas was obtained by allowing the sample to remain at 4.2 K for about 90 min and then suddenly heating it. The results agree in the temperature region where both methods are applicable. After a change in temperature, changes in the area of the NMR line were measured for a period of about 90 min. (No spin conversion is expected to occur for the rotationally hindered molecules, because the temperature is much larger than the splittings between the tunneling levels for these molecules. Thus the very long conversion time associated with these molecules has no influence on the current measurements.)

Van Hecke and Van Gerven[2] fitted their observations of the relaxation of the nuclear susceptibility to a linear increase to its final value, implying a zeroth-order rate law. Subsequently, Piott and McCormick[3] attributed the apparent departures from exponential relaxation at temperatures of 4.2 K and below to a difference between the E to F and the F to A conversion rates. However, this would lead to a faster initial conversion rate, rather than the slower initial rate they appear to have observed. The conversion for temperatures above 4.2 K is well described by a simple exponential relaxation

$$A(t) = C_1[1 + C_2 \exp(-t/\tau)] \ . \tag{1}$$

Here $A(t)$ is the time-dependent area of the NMR line and C_1 and C_2 are arbitrary constants. We shall call τ the spin-species conversion time. Our data were fitted to this functional form using a nonlinear least-squares procedure.

Figure 1 shows the spin conversion times obtained in this manner, as a function of temperature. For temperatures below the phase transition temperature (20.4 K), we may assume that the rotationally hindered molecules make no contribution to the observed conversion rate. We observe no statistically significant change in the conversion rate upon warming through the transition. To within experimental error, our measurements agree with previous NMR measurements at temperatures of 6 K and below.[3] Similarly, our high-temperature measurements are consistent with the neutron cross-section measurements of Lushington and Morrison.[5]

In order to calculate the temperature dependence of the single-phonon emission processes considered by Nijman and Berlinsky,[8] we must add the stimulated emission due to thermal phonons. The result is

$$\tau(T) = \tau(0)\{1 + 2[\exp(E_{FA}/kT) - 1]^{-1}\}^{-1} \ . \tag{2}$$

Here k is the Boltzmann constant and E_{FA} is the splitting between the lowest levels for F- and A-type molecules (12.7 K). In Fig. 1, the dashed line shows the conversion time calculated from Eq. (2), with $\tau(0)$ adjusted to reproduce the experimental conversion time at 4.2 K, our lowest temperature. Note that the only effect of changing $\tau(0)$ is to shift the calculated curve vertically, because of the logarithmic scale in Fig. 1.

It is clear that the conversion time has a much stronger temperature dependence than is consistent with the direct phonon emission mechanisms. Nijman and Berlinsky[8] have suggested that the thermal excitation of librons will provide an additional conversion mechanism for T above about 10 K. The temperature dependence of such a process should be dominated by a Boltzmann factor for the excitation of the librons. Accordingly, we have fitted the measured conversion times to the functional form

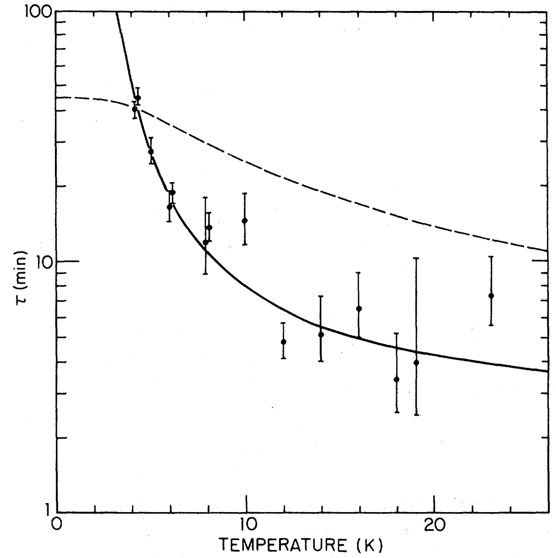

FIG. 1. Measured spin-species conversion time τ vs temperature (data points). The dashed line shows the temperature dependence expected for a phonon emission process, adjusted to agree with the measured time at 4.2 K. The solid line shows the best fit to the functional form expected for a process mediated by thermal excitations.

$$\tau(T) = \tau(\infty)\exp(T_0/T) \ . \tag{3}$$

The result of this fit is $\tau(\infty) = 2.29$ min, $T_0 = 12.4$ K. The solid line in Fig. 1 shows the conversion time calculated from Eq. (3) with these parameters. The barrier height T_0 is much less than the energy of the librons associated with the rotationally hindered molecules (about 70 K), but it is comparable to the energy of the excited states of the free-rotor molecules.[6]

This suggests that spin-species conversion in CH_4 at liquid-helium temperature and above is dominated by a process dependent upon the thermal excitation of the free-rotor molecules. A detailed theory of such processes has not yet been developed.

ACKNOWLEDGMENT

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