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NMR direct detection of tunnel splittings in solid SiH_4

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A magnetic-field cycling technique is used to detect the tunnel energy splittings of the ground librational state of solid SiH_4 in its low-temperature phase. New in the present experiment is the use of the nuclear (proton) Zeeman splitting (unlike the electron Zeeman splitting of an impurity as in previous experiments) to match the tunnel splittings by means of the external magnetic field. The resonant exchange of energy between tunnel and spin system is observed through the occurrence of peaks in the proton spin-lattice relaxation rate versus magnetic field. The peak pair observed at high fields is associated to the A-T tunnel splitting and has a value of 0.22 μeV. The peak pair at low fields is ascribed to the T-T splitting arising from a lower than tetrahedral symmetry and has a value of 0.033 μeV. The measured splittings are temperature independent below 15 K; they slightly decrease with increasing temperature above 15 K. Around 20 K all resonant peaks in the spin-lattice relaxation rate vanish without noticeable broadening.

I. INTRODUCTION

The rotational behavior of molecules, molecular groups, or ions in the solid phase ranges from the nearly free rotor (like H_2) to completely ordered phases (NH_4Cl), depending on whether the orienting potential is much smaller or much larger than the rotational constant. In the latter case, the molecules perform librations around their equilibrium orientations. For intermediate ordering potentials, the librational states are split by tunneling motion between the different potential wells associated to the equilibrium orientations. Methane in the low-temperature phase was shown to be a mixed case where $\frac{1}{4}$ of the molecules behave as free rotors and $\frac{3}{4}$ as oriented molecules with tunnel splittings in the 0.1-meV range.[1]

Very little, however, is known about the molecular state of SiH_4, the analogous tetrahedral molecule, especially at temperatures below the phase transition ($T = 63.45$ K). Recent NMR measurements[2-5] show evidence that tunneling motion dominates the low-temperature properties of this molecule: the proton second moment is much smaller than expected for a rigid tetrahedron and the spin-lattice relaxation time T_1 shows a nonclassical minimum around 12 K. To our knowledge, no data are available on the symmetry of the crystal field nor on the value of the tunnel energy splittings in solid SiH_4. A tetragonal unit cell has been proposed for phase I ($T > 63.45$ K) and a lower (undetermined) symmetry for phase II.[6] Neutron-diffraction studies on SiD_4 remained as well inconclusive as to the crystal structure of the low-temperature phase but they too clearly showed that solid silane is of a lower symmetry than solid methane.[7]

One can reasonably expect the larger SiH_4 molecule to be rotationally more hindered than CH_4 and hence, to have much smaller tunnel splittings. Actually, no conversion of nuclear spin species like in CH_4 could be observed in SiH_4,[2,4] indicating that the tunnel energy splittings are indeed much smaller than a few degrees Kelvin. Hüller *et al.*[8] have developed a variational method to treat rotational excitations of molecular solids in any potential strength. Their explicit calculations of the rotational energy levels of the CH_4 molecule reorienting in a tetrahedral potential agree very well with the experimental results from neutron scattering experiments on CH_4.[1] Using their theoretical results for the ground-state tunnel frequencies of a tetrahedron in a tetrahedral potential we made a calculation of the tunnel splittings of the librational ground state of the SiH_4 molecule, in the assumption of a tetrahedral crystal field. From the known rotational constant ($B = 1.04 \times 10^{-22}$ J) and the temperature of the phase transition ($T = 63.45$ K) of SiH_4 we then predict a ground-state A-T tunnel splitting of about 0.3 μeV. Due to the assumptions made here we emphasize that this number is not more than a crude estimate of the tunnel splitting. Nevertheless, one readily concludes from its order of magnitude, that such small energy splitting is—at least in the present stage—hardly accessible to neutron scattering spectrometers. However, expressed on the frequency scale, the value of this splitting is about 72 MHz, which puts it into the radio-frequency range and more particularly into the frequency range normally accessible to the NMR spectroscopist. This brought us to set up an experiment to search for and detect these tunnel levels using nuclear-magnetic-resonance spectroscopy.

II. NMR FIELD CYCLING EXPERIMENT

The basic idea is to sweep the external magnetic field and look for resonant effects in the spin system occurring when the nuclear Zeeman splitting matches the tunnel splitting of the librational ground state, leading to the resonant exchange of energy between the nuclear spin system and the orientational degrees of freedom (lattice). The occurrence of resonance is monitored via direct observation of the partially relaxed z component of the nuclear magnetization as further described below.

Our experiment has some analogy with that of Glättli[9] for the detection of tunnel splittings in CH_4, in the GHz range. In the latter, however, the Zeeman splitting of the electron-spin system of impurities created by irradiation is tuned to the tunnel splitting; hereby the nuclear-spin species conversion rate is monitored through the measurement of the proton T_1 as a function of time during conversion. Closer to our technique is the measurement of the magnetic-field dependence of the proton T_1 in γ-irradiated 4-methyl-2,6-ditertiarybutylphenol by Clough *et al.*[10] A peak is observed at the frequency where the Zeeman splitting of the unpaired electron matches the tunnel splitting (GHz range) of the CH_3 group, providing an efficient path for the spin-lattice relaxation of the protons. Also, Jones *et al.* reported a level-crossing experiment[11] where the tunnel splitting in hexamethylbenzene ($\omega_t/2\pi = 11.2$ MHz) is detected indirectly by measuring the amplitude of the magnetization after an adiabatic magnetization, and comparing it with the amplitude of the high-field magnetization.

In our experiment, the relevant parameter is the proton spin-lattice relaxation rate $1/T_1$. For a tetrahedral molecule in a tetrahedral crystal field the librational ground state splits into a fivefold degenerate A level (total proton spin $I = 2$), a ninefold degenerate T-level ($I = 1$), and a twofold degenerate E level ($I = 0$),[12] as shown in Fig. 1. Using symmetry-adapted wave functions and operators, the proton spin-lattice relaxation rate of SiH_4 in the ground librational state can be written (common spin-temperature assumption)[13]

$$1/T_1 = \omega_D^2 (R_{T-T} + R_{T-A} + R_{E-A}) \ , \tag{1}$$

where R_{i-j} is the transition rate between the Zeeman levels of the i and j tunnel states ($i,j = A,T,E$) induced by intramoleculear dipolar interaction. The terms associated to the E-T, respectively, A-A transitions are zero as the corresponding terms of the intramolecular dipolar Hamiltonian vanish. For the particular case of SiH_4 and in the temperature range under consideration one has $E_E, E_T << kT$. Assuming a powder, one then calculates, from Ref. 13,

$$R_{T-T} = \tfrac{2}{5}[J^E(\omega_0) + \tfrac{8}{5}J^E(2\omega_0) + \tfrac{3}{5}J^T(\omega_0) + \tfrac{12}{5}J^T(2\omega_0)] \ , \tag{2}$$

$$R_{T-A} = \tfrac{9}{10}[J^T(\omega_T + \omega_0) + J^T(\omega_T - \omega_0)] + \tfrac{36}{10}[J^T(\omega_T + 2\omega_0) + J^T(\omega_T - 2\omega_0)] \ , \tag{3}$$

$$R_{E-A} = \tfrac{2}{10}[J^E(\omega_E + \omega_0) + J^E(\omega_E - \omega_0)] + \tfrac{8}{10}[J^E(\omega_E + 2\omega_0) + J^E(\omega_E - 2\omega_0)] \ , \tag{4}$$

and

$$\omega_D^2 = \tfrac{9}{64}(\gamma^2 \hbar / r^3)^2 \quad (\text{for } SiH_4,\ \omega_D^2 = 4\times 10^8 \text{ sec}^{-2}) \ ,$$

with

$$J^i(\omega) = 2\tau_i/(1 + \omega^2 \tau_i^2) \quad \text{and} \quad \hbar\omega_i = E_i \ .$$

τ_i can be written in terms of the correlation times τ_3 and τ_2 for reorientation of the tetrahedron about the threefold, respectively, twofold symmetry axis[14]

$$1/\tau_E = 12/\tau_3 \quad \text{and} \quad 1/\tau_T = 8/\tau_3 + 4/\tau_2 \ .$$

Equations (1)–(4) clearly exhibit all "resonant" features on which the field cycling experiment as described below, is based. A detailed discussion of the cases $\omega_0 >> \omega_T, \omega_E$ and $\omega_0 << \omega_T, \omega_E$ including symmetry- and energy-restricted spin diffusion can be found elsewhere.[13]

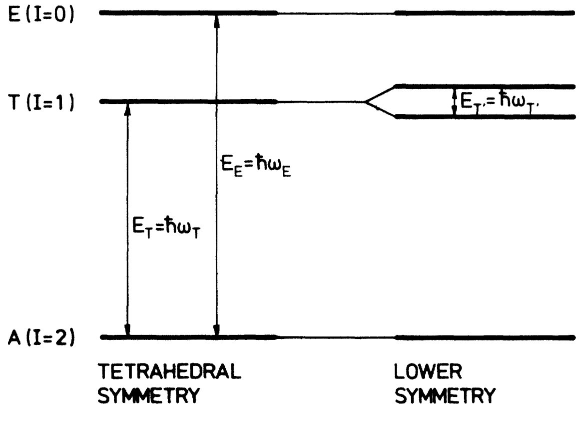

FIG. 1. Energy-level scheme for the SiH_4 molecule in the ground librational state for tetrahedral and for lower symmetry of the crystal. For the lowest symmetry the T manifold splits into three sublevels. I is the total proton spin.

In the low-temperature range where the field cycling experiment is performed, one has ω_0, ω_E, and $\omega_T >> 1/\tau_i$ $(i = E,T)$. It then follows from Eqs. (1)–(4) that when the Larmor frequency ω_0 of the proton spins, which is set by the value of the external magnetic field $H_0 (\omega_0 \equiv \gamma H_0)$, is such that

$$n\omega_0 = \omega_E \text{ or } \omega_T \quad (n = 1,2) \tag{5}$$

(level-crossing condition), one has a very efficient relaxation mechanism for the spin energy, resulting in the occurrence of a maximum in $1/T_1$.

The actual field-cycling experiment then goes as follows. The proton magnetization is saturated by a train of radio-frequency pulses in the "reference" static magnetic field at resonance (typically 1.4 T). The magnetic field is then quickly brought to a new value H (in about 15 sec for any field change), where the nuclear magnetization is allowed to relax for a time $t < T_1$ (typically 1 min). The magnetic field is then quickly brought back to its resonance ("reference") value where the amplitude of the partially relaxed proton magnetization $M_z(t)$ is measured after a 90° pulse. This field cycle is then repeated for different values of the magnetic field (here, between 0.01 and 1.8 T). Field cycles taken with different values of the reference field showed—as expected—that the results are independent of the reference field. An increase in the relaxation rate is then monitored as an increase in $M_z(t)$. Of course, t has to be taken smaller than T_1 at any field, in order to observe a resonant effect in T_1 via an increase in $M_z(t)$.

For these experiments we used a Bruker 321s pulse spectrometer together with a Bruker-Hall field regulation unit B-H11 to cycle and stabilize the magnetic field. The temperature was kept within better than 1% of its nominal value, without regard to the length of the field-cycling experiment. Matheson research-grade SiH_4 gas was condensed at 77.4 K in a 7.5-mm-o.d. glass sample tube and sealed off.

III. RESULTS AND DISCUSSION

A typical result of a complete field-cycle run is shown in Fig. 2 ($T = 8.8$ K). In order to compare the results at different temperatures, the quantity $M_z T/C$, instead of M_z, has been plotted; C is the Curie constant. The experimental results clearly demonstrate the pairwise occurence [field ratio 2:1, see Eq. (5)] of strong resonance peaks in the magnetization and hence, in the relaxation rate. They confirm our prediction—based on the crude estimate made under I—that our NMR technique can find the tunnel splittings for the SiH_4 molecule in the MHz frequency range.

The bending of the magnetization curve at higher fields, in other words, the departure from the Curie law is due to the dependence of T_1 on the magnetic field. The z component of the proton spin magnetization at a time t after saturation follows the expression

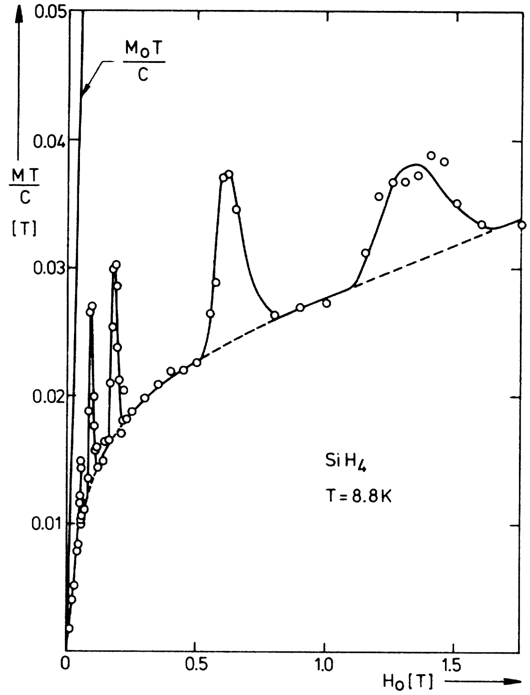

FIG. 2. Field-cycling experiment in SiH_4. The reduced magnetization MT/C (C is the Curie constant) is plotted vs the external magnetic field H ($T = 8.8$ K). The reference field is 0.9 T ($\omega_0/2\pi = 38.2$ MHz). The straight line (high slope) represents $M_0 T/C$, where M_0 is the proton magnetization at thermal equilibrium.

$$M_z(t) = (C/T)H[1 - \exp(-at/H^n)] \ .$$

[To a first approximation $n = 2$. In our further analysis, a more elaborate expression was used for $T_1(H)$, which however is not relevant for the present discussion.] If we would take t long enough, $M_z(t)$ would keep following a Curie law. This, however, conflicts with the condition $t < T_1$ required for the observation of any effect as described above.

$M_z(t)$ is seen to display two strong peaks at fields $H = 0.63$ and 1.26 T. These we associate with the resonance condition $2\omega_0 = \omega_T$ and $\omega_0 = \omega_T$, respectively [Eq. (5)], yielding $\omega_T/2\pi = 53.6 \pm 2.5$ MHz or $E_T = 0.22 \pm 0.01$ μeV. Although we extended our measurements up to 1.8 T, the resonance condition $n\omega_0 = \omega_E$ (expected to occur at $\omega_E = \frac{3}{2}\omega_T$ for tetrahedral symmetry[8] and at smaller values for lower symmetry) is not seen for the following reason. From our T_1 measurements taken at different frequencies as a function of temperature[15] we deduce that reorientational motion around twofold axes dominates, so that

$1/\tau_2 >> 1/\tau_3$ or $1/\tau_E << 1/\tau_T$. In the low-temperature region of interest here ($\omega\tau_i >> 1$) this results in $J^E(\omega) << J^T(\omega)$ and hence in $R_{E\text{-}A} << R_{T\text{-}A}$ according to Eqs. (3) and (4). It is worth pointing out that neither in CH_4,[9] nor in $(NH_4)PbCl_6$,[16] this E-A transition was never clearly observed.

Until now we assumed a tetrahedral site symmetry for the SiH_4 molecule. As pointed out in Sec. I a lower symmetry is more likely. A lowering of the site symmetry partially or totally lifts the degeneracy of the T manifold (Fig. 1). The contribution of $R_{T\text{-}T}$ to the relaxation rate $1/T_1$ [Eq. (2)] now shows additional maxima as a function of the external magnetic field $(H_0 \equiv \omega_0/\gamma)$, at

$$n\omega_0 = \omega_{T_{ij}}' \quad (n=1,2) \quad ,$$

where $\hbar\omega_{T_{ij}}'$ is the energy difference between the sub-levels T_i and T_j of the T manifold. The number of these sub-levels (min 2, max 3) and their energy difference depends on the symmetry of the site. This splitting of the T levels due to a lower than tetrahedral symmetry is believed to account for the occurrence of the lower field peaks (Fig. 2) of which the well-resolved pair at 0.095 and 0.19 T respectively, can unambiguously be assigned to $2\omega_0 = \omega_{T'}$ and $\omega_0 = \omega_{T'}$, respectively, yielding $\omega_{T'}/2\pi = 8.1 \pm 0.4$ MHz or $E_{T'} = 0.033 \pm 0.002$ μeV. This splitting of the T level also accounts for the broadening of the T-A peaks at 0.63 and 1.26 T. Whether the weaker peak(s) in Fig. 2 result from further splitting of the T manifold is highly speculative as finding pairs of peaks matching exactly the 2:1 field ratio turns out to be unsuccessful (even by including one of the above mentioned peaks). A T level splitting into two sublevels (the lowest one being twofold degenerate) would indicate a D_{2h} site symmetry.

As to the width of those peaks in $1/T_1$, it was already mentioned that the high-field peak pair is broadened by a partial lifting of the degeneracy of the T manifold, giving rise to the low-field peak pair. Besides, all peaks are broadened by a distribution of tunnel frequencies among the crystallites of the powder sample. Both these sources of inhomogeneous broadening lead to the 2:1 ratio also observed in the width of the peaks of the high- and low-field peak pair, respectively.

All measurements were performed at temperatures low enough for T_1 to be dominated by the lowest molecular (librational) state and hence, by tunnel properties. Our field cycling experiments performed as a function of temperature (1.8–25 K) show that all resonant peaks in $1/T_1$ disappear above 20 K, without noticeable broadening. The value of the magnetic field at which these peaks occur, in other words, the value of the tunnel splittings, remain temperature independent up to 15 K and slightly decrease with increasing temperature above 15 K until they disappear around 20 K (Fig. 3). It should be emphasized that above 15 K the 2:1 ratio in the position of the peaks as a function of the field remains strictly constant, supporting the validity of the present experiment based on Eqs. (1)–(4).

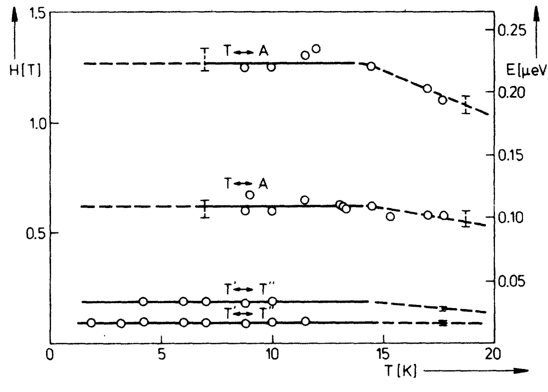

FIG. 3. Temperature dependence of the resonant peaks in the relaxation rate at $n\omega_0 = \omega_T$ (A-T transition) and $n\omega_0 = \omega_{T_{ij}}'$ (T'-T'' transition), where $n = 1, 2$. Above 20 K all peaks disappear. The width of the peaks is temperature independent.

Finally, all splittings deduced from this field cycling experiment account very well for the nonclassical behavior of the spin-lattice relaxation time T_1 as a function of temperature and frequency below 20 K.[5,15] In connection with the energy-level scheme presented here and with the assumption of the ground librational state made earlier, we like to point out that the activation energy of the correlation time τ at these low temperatures is calculated from our experiments[15] to be about 62 K, a value which can be related to the energy difference between the ground and first-excited librational level.

IV. CONCLUSION

We believe that the use of a field-cycling experiment like the one reported here for a direct detection of resonant effects between tunnel and nuclear Zeeman energy splittings is very promising for all compounds where tunnel splittings are expected to be found in the MHz range (typically, 0.005–0.5 μeV). It is much more accurate and straightforward than a level crossing experiment using adiabatic magnetization[11] or than a full T_1 measurement as a function of frequency and temperature.[16]

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