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Theory of Nuclear Spin Conversion in the β Phase of Solid Methane

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The dominant mechanism for spin conversion in solid CH_4 in the β phase is found to be a hybrid process in which intramolecular dipolar interactions mix the nuclear spin states, and the intermolecular octupole interaction, modulated by phonon emission, causes transitions between orientational states. The conversion rate calculated for free rotor molecules is 31 to 54% per hour. The mechanism is shown to be inefficient for ordered molecules which are estimated to convert at least 1000 times slower.

In this Letter we report the first theoretical calculations of the nuclear spin conversion rate in solid CH_4. Our calculations apply specifically to the partially ordered β phase which has been the subject of several experimental[1-10] and theoretical[11-14] studies and in which one might expect the details of the spin isomer composition to play a crucial role. Two important new results have emerged from this work. First we have identified the dominant mechanism for conversion as one involving the *intra*molecular dipole-dipole interaction H_{dd}^{intra}, which mixes the nuclear states, in conjunction with the *inter*molecular octupole-octupole interaction, modulated by phonon emission, which causes the rotational transition. We find this process to be about 30 times faster than that involving intermolecular dipole-dipole interactions H_{dd}^{inter}. Second, we have shown that fast conversion ($\tau \simeq 2$ h) occurs only on the free-rotor molecules while conversion of the ordered molecules is much slower. This is mainly because the off-diagonal matrix elements of the octupole-octupole interaction are very small for ordered molecules. In addition, the larger mixing of these closely spaced levels (see Fig. 1) by H_{dd}^{intra} is more than cancelled by the smaller density of final phonon states.

Our results are consistent with existing experimental data,[1-3] and the possibility that fast conversion occurred only on the freely rotating molecules had been suggested earlier on the basis of NMR measurements.[4,5] However, this suggestion was not widely accepted, and the mechanism which could lead to such a great difference in conversion rates remained obscure. The most attractive feature of our work is that in establishing the probable mechanism for conversion, i.e., one which accounts quantitatively for the observed time constant of the free-rotor molecules, we obtain in a natural way an explanation for the difference in conversion rates of ordered and disordered molecules. In addition, several of our arguments, namely, those concerning possible spin conversion mechanisms, the dependence of the conversion rate upon the phonon spectral density, and the smallness of off-diagonal matrix elements of purely spatial operators between tunneling states, should also apply to spin conversion in CH_3 groups.

The β phase of solid methane was first predicted in 1959 by James and Keenan[11] on the basis of a classical model of interacting octupoles on a face-centered cubic lattice. The structure consists of eight sublattices. The molecules on six of these sublattices are ordered in such a way that their octupole interactions with molecules on the other two sublattices add to zero, and thus

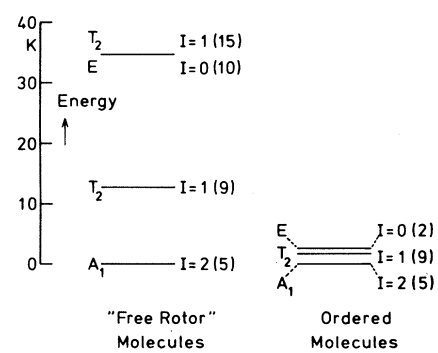

FIG. 1. Energy level diagram for the low-lying states in the β phase of solid CH_4. The T-A splitting is 12.7 K for the nearly free rotors and 1.6 K for the oriented molecules. In this calculation the A, T, and (T,E) "free-rotor" states are approximated by true free-rotor states with $J=0$, 1, and 2, respectively.

the molecules on these two sublattices rotate freely.

In 1972 Press[6] established, by neutron scattering, that the β phase of solid CD_4, and by inference the low-temperature phase of CH_4, did in fact correspond to the James and Keenan structure. Later Press and Kollmar[7] determined the energy levels of both the nearly free-rotor molecules and the tunnel splittings of the ordered molecules. Using this energy level scheme, Code and Higgenbotham[4] were able to interpret the NMR results[4,5] in terms of a model in which the freely rotating molecules converted rapidly ($\tau \simeq 1$ h), while no conversion occurred in the ordered molecules. Fast conversion of the freely rotating molecules can also be inferred from the second moment measurements of Nijman and Trappeniers.[8,9]

Energy levels for the low-lying states in the β phase are shown in Fig. 1. The symmetry labels A, T, and E correspond to $I=2$, 1, and 0, respectively. In the calculations which follow, the spatial wave functions of the "free-rotor" molecules are approximated by true free-rotor wave functions. The spatial wave functions of the oriented molecules are taken to be angular δ-function distributions of the appropriate symmetries. The first process which we consider is that involving H_{dd}^{inter} modulated by phonon emission. We note that it is the *gradient* of the dipolar field which causes transitions between states of different I. Then the lowest-order term in the expansion of H_{dd}^{inter} which is effective in causing conversion is

$$H_{dd}^{(1)} = \sum_{\delta,p} (\vec{u}_\delta \cdot \nabla)(\vec{r}_p \cdot \nabla) H_{dd}^{\text{inter}}, \tag{1}$$

where δ is summed over nearest neighbors of the molecule which is to convert, and which we take as our origin; $\vec{u}_\delta$ is a small relative displacement of molecule δ with respect to that at the origin; and $\vec{r}_p$ is a vector from the center of the carbon atom of the central molecule to one of its four protons ($p=1,\ldots,4$). Since the intermolecular distance R_0 is much larger than $|\vec{r}_p|$ we make the reasonable approximation that the total nuclear spins I_δ of the neighboring molecules are localized on their respective carbon atoms. Then the conversion rate from species T ($I=1$) to species A ($I=2$) is

$$R_{T\to A} = (2\pi/\hbar)\sum_{i,f} P_i(T)\,|\langle f(A)|H_{dd}^{(1)}|i(T)\rangle|^2 \delta(E_i - E_f). \tag{2}$$

Treating the nine T states as degenerate and assuming that only the lowest T and A states are occupied, we have $P_i(T)=\frac{1}{9}$. The initial state is assumed to contain no phonons.

The remainder of the calculation proceeds in a manner quite similar to that of the corresponding calculation for solid H_2.[15] However, the rather complicated symmetry of the methane molecules necessitates the use of a more formal group-theoretical approach involving Clebsch-Gordan coefficients of the tetrahedral group as well as those of the full rotation group. The phonons enter the transition-rate formula in the form of the correlation function

$$G_{\delta\delta'}^{\mu\mu'}(E_{T-A}) = R_0^{-2} \sum_{\vec{K},\tau} \langle 0|u_{\delta'}^{\mu'}|\vec{K},\tau\rangle\langle\vec{K},\tau|u_\delta^{\mu}|0\rangle\,\delta(E_{T-A} - E_{\vec{K},\tau}), \tag{3}$$

where $\vec{K}$, τ specifies a one-phonon state. Since the energies of the transitions are small compared to the Debye energy E_D, it is reasonable for this problem to use an isotropic Debye model which leads to the result

$$G_{\delta\delta'}^{\mu\mu'}(E_{T-A}) = \delta_{\mu\mu'} \frac{3}{E_D^3} \frac{\hbar^2}{2MR_0^2} E_{T-A}[1 - 2j_0(x) + j_0(xR_{\delta\delta'}/R_0)], \tag{4}$$

where M is the mass of CH_4, v is the sound velocity, $x = E_{T-A}R_0/\hbar v$, $\vec{R}_{\delta\delta'} = \vec{R}_\delta - \vec{R}_{\delta'}$, and $j_0(x)$ is a spherical Bessel function. After a tedious calculation, and taking $E_D = 75$ K[6] and $E_{T-A} = 12.7$ K,[7,10,14] we obtain a conversion rate of 0.7%/h for the free-rotor molecules, which is about two orders of magnitude smaller than the observed rate.[1-3]

The conversion rate for ordered molecules by this mechanism is 1.6×10^{-3}%/h which is very slow. The difference results mainly from the phonon spectral function which goes like the cube of E_{T-A} for $E_{T-A} \ll E_D$. Thermal population of phonon states will enhance the rate by about a factor of 5 at 42. K. This mechanism also applies to conversion by means of O_2 impurities. A crude estimate based simply on the relative strength of the magnetic moments gives a conver-

sion time of about 10 min for an ordered molecule with a single O_2 neighbor.[16]

The second conversion process involves H_{dd}^{intra} together with the intermolecular octupole-octupole coupling H_{oo}. For free-rotor molecules, the dipolar coupling mixes $I=1, J=2$ states with the $I=2, J=0$ final states, and $I=2, J=3$ states into the $I=1, J=1$ initial states. The $(I=1, J=1)$ T states are not mixed into the ground state by H_{dd}^{intra} because the spatial part of this matrix element is zero. Other higher-order processes will also contribute to the mixing. In particular we note that the crystal field, which acts on the "free-rotor" molecules and causes their energies to differ from the free-rotor values, will mix the $J=2$ and $J=1$ states, and this admixture can then be mixed into the ground state by H_{dd}^{intra}. It is difficult to estimate the size of this effect, but we expect it to be smaller than the direct process. For simplicity, we consider first the conversion rate which results from mixing in the final state.

Conversion occurs when the phonon-modulated octupole-octupole coupling, $H_{oo}^{(1)}$, induces transitions between the $I=1, J=1$ state and the small admixture of $I=1, J=2$ in the ground state. $H_{oo}^{(1)}$ is defined as

$$H_{oo}^{(1)} = \sum_{\delta} \vec{u}_{\delta} \cdot \nabla H_{oo}, \tag{5}$$

and contains no spin operators. The conversion rate for this process is given by

$$r_{T\to A} = \frac{2\pi}{\hbar} \sum_{i,f} P_i |\xi_f|^2 \langle f(A)|H_{oo}^{(1)}|i(T)\rangle|^2 \delta(E_i - E_f), \tag{6}$$

where ξ_f is the mixing coefficient for the $I=1, J=2$ state, with the same nuclear quantum numbers as the initial state, into the final state. ξ_f is proportional to $H_{dd}^{\text{intra}}/\Delta E_{0\text{-}2}$. The final result for the free-rotor conversion rate is

$$r_{T\to A}' = \left(\frac{117}{7}\right)^2 \left(\frac{d_D}{E_{0\text{-}2}}\right)^2 \left(\frac{\Delta}{E_D}\right)^2 \frac{\hbar^2}{2MR_0^2 E_D} \frac{E_{T\text{-}A}}{\hbar} \{0.3426[1 - j_0(2x)] + 0.0286[j_0(x) - j_0(\sqrt{3}x)]\}, \tag{7}$$

where d_D is the intramolecular dipolar coupling constant ($d_D = 1.02\times10^{-6}$ K), and $\Delta = (2079\pi/325)^{1/2}\Omega^2/R_0^7$, where Ω is the octupole moment of a methane moelcule. A straightforward calculation shows that the effect of mixing $J=1$ and $J=3$ in the initial states leads to an additional rate given by $(\Delta E_{0\text{-}2}/\Delta E_{1\text{-}3})^2 r_{T\to A}$. Using the theoretical value for the ratio of rotational splittings,[14] we obtain a 39% enhancement of the rate from this mechanism.

All of the parameters in Eq. (7) can be estimated with reasonable accuracy except for the octupole moment Ω which is difficult to determine experimentally and for which no accurate theoretical calculations exist. The most reliable experimental values are probably those of Ozier and Fos,[17] $|\Omega| = 2.6\times10^{-34}$ esu, from collision-induced infrared absorption, and of Bose, Sochanski, and Cole[18] from dielectric virial coefficient measurements and Snook and Spurling[19] by a variety of techniques which give $|\Omega| = 3\times10^{-34}$ esu. These values of $|\Omega|$ lead to conversion rates of 31 to 54% per hour, somewhat slower than the experimental values which range from 50 to 130% per hour.[1-3,5] We note, however, that the experimental values represent an upper bound on the intrinsic rate because of the important effect of oxygen impurities on conversion.

The calculation for the ordered molecules proceeds in a similar way. H_{dd}^{intra} causes mixing between the low-lying A, T, and E states. Nevertheless, the probability of transitions between these mixed states via the octupole-octupole interaction is identically zero in this approximation in which the localized states are described by angular δ functions. To see this we note that for perfect molecular ordering any purely spatial operator is proportional to the unit matrix. The "mixed" states, which result from the interaction H_{dd}^{intra}, are related to the unperturbed states by a unitary transformation, which, of course, also preserves the form of unit operators such as H_{oo}. Consequently such operators cannot lead to transitions between the perturbed states.

The actual conversion rate for the ordered molecules depends on the finite overlap of the localized wave functions. We have estimated this overlap using the formulas of Nagamiya[20] for the energies of the ordered molecules, the observed values of their splittings,[7] and theoretical estimates of the average energy of these states.[14] We find the overlap integral to be about 1.3×10^{-2}. Taking into account, also, the stronger mixing of the closely spaced levels of the ordered molecules and the smaller value of the phonon spectral function, we obtain an overall estimate that conversion by this mechanism is roughly 2×10^{-4}

times that of the free-rotor molecules. This is still faster than the rate due to H_{dd}^{inter}, and thus it is probably this mechanism which determines the conversion rate of the ordered molecules, giving a ($T=0$) conversion time on the order of a year.

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Orientational Order in Biaxial Liquid Crystals

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^{14}N nuclear-quadrupole-resonance data show that the electric-field-gradient tensor at the ^{14}N sites in terephthal-*bis*-butylaniline deviates from cylindrical symmetry in the biaxial smectic-*C*, smectic-*H*, and smectic-VI phases whereas it is cylindrically symmetrical in the uniaxial smectic-*A* phase. The results suggest that in the smectic-*C* phase the molecular tilt induces the rotational bias and not vice versa, whereas in the smectic-*H* phase the situation is different and the results may be interpreted within the Meyer-McMillan model.

There has been considerable interest recently in the nature of the local orientational order in the biaxial smectic liquid crystalline phases. According to the Meyer-McMillan theory,[1] the tilting of the molecules with respect to the smectic planes in the smectic-*C* and the smectic-*H* phases is connected with a freezing out of the "isotropic" rotational motion of the molecules around their long axes due to the antiparallel, antiferroelectriclike ordering of the "outboard" molecular dipoles.[1] The discovery of ferroelectricity in chiral smectic-*C* phases,[2] where the in-plane spontaneous polarization seems to arise from a small but nonvanishing parallel ordering of molecular dipoles—and a resulting rotational bias—, has lent further support to this model. The freezing-out of the molecular rotations around their long axes is, however, not a necessary condition for the occurrence of biaxiality in smectic systems and alternative models have been formulated[3] where the tilt takes place while the molecules are still freely rotating.

The experimental evidence for the local orientational order predicted by the Meyer-McMillan theory[1] in achiral biaxial smectics has been so far either inconclusive or negative. Proton[4] and deuteron[5] magnetic resonance measurements in terephthal-*bis*-butylaniline (TBBA) as well as x-ray[6] and quasielastic neutron scattering[7] data have all been interpreted in terms of rapid and nearly or completely "isotropic" rotational motion of the molecules around their long axes. Only a recent magnetic resonance experiment[8] on the terminal methyl-group deuterons in *n*-heptyl-