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Publication Date
1976-09-01

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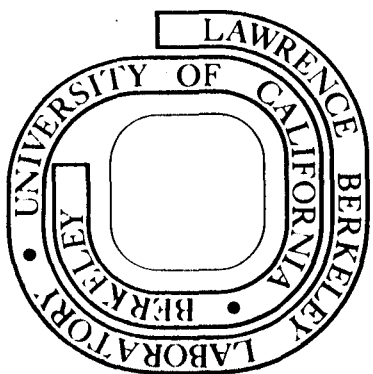
Janice J. Kim and Kenneth S. Pitzer

September 1976

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CRYSTAL FIELD EFFECTS ON OXYGEN IN SOLID METHANE AND

THE CATALYSIS OF SPIN-SPECIES CONVERSION OF METHANE

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(ABSTRACT)

The energy states are calculated for an
oxygen molecule in a crystal field of cubic symmetry
such as would be appropriate for a substitutional
site in solid methane. The resulting heat capacity
is also calculated and discussed in relation to
data for oxygen-doped methane. The catalytic
effect of oxygen on the spin-species conversion of
methane is treated by consideration of the dipole-
dipole interaction of the electron spin of oxygen
with the proton spin of methane. The matrix elements
are calculated for the low-energy states of methane
and of oxygen. It is found that oxygen should be
an effective catalyst for spin-species conversion
above about $0.3°K$ but that its effectiveness may
decrease rapidly below that temperature.

I. Introduction

The addition of a small amount of paramagnetic substance such as oxygen has been found to facilitate the conversion of nuclear-spin species. Early studies on the kinetics of the ortho-para hydrogen conversion process noted that oxygen and other paramagnetic molecules greatly enhanced the conversion rate.[1]

The phenomenon of nuclear-spin-species conversion in solid methane has been observed in the low-temperature phase (1-20°K) using a variety of techniques including nuclear magnetic resonance, level-crossing experiments, and heat capacity measurements.[2] The Pauli principle allows the existence of only certain nuclear spin states with a given rotational state to preserve the overall symmetry of the total wave function. In solid methane above the transition near 20.4°K all of the molecules undergo somewhat restricted rotation.[3] Below this transition,[4] however, three-fourths of the molecules are rather strongly oriented in a cog-wheel manner in sites of D_{2d} symmetry while the remaining one-fourth of the molecules rotate rather freely in sites of O_h symmetry. The molecular centers lie on a face-centered cubic lattice both above and below 20.4°K.

While various methane-methane interactions, e.g., spin-spin and spin-rotation, induce interspecies conversion, these processes are very slow at very low temperatures. In an effort to reduce relaxation times in low-temperature studies of methane, small quantities of oxygen were often introduced into the lattice to obtain more rapid equilibrium.

Vogt and Pitzer[2 f,g] have recently reported low tempera-
ture heat capacity studies of methane containing approximately
0.8% oxygen. An anomaly observed in the region about 1°K is
attributed to spin-species conversion. The present theoretical
work[5] was undertaken to further interpret these and other
experimental studies of oxygen-doped methane.

In Section II calculations are presented concerning the
properties of oxygen in a cubic lattice such as methane.
Included are calculations of the heat capacity for various
cubic fields as well as for freely rotating molecules. These
results indicate that corrections to the heat capacity of
typical oxygen-doped methane samples will be small and that
values from the freely rotating model will be a good approxi-
mation for cubic fields of moderate strength.

Section III treats the problem of spin-species conversion
of methane by interaction with oxygen. The results are
discussed in Section IV with particular reference to con-
version rates below 1°K.

II. Properties of O_2 in a Cubic Lattice

As oxygen-methane samples are solidified, it is likely
that oxygen will occupy a methane site in the lattice structure.
The carbon atoms of the methane lattice form a face-centered
cubic structure. Since oxygen is smaller than a methane
molecule, it may be rather freely rotating in the methane
lattice, and we choose as our model that of a rotating oxygen
molecule perturbed by a crystal field of cubic symmetry.

The spectrum of the ground electronic state of gaseous
oxygen ($^3\Sigma_g^-$) shows a fine structure splitting of the rotational
levels.[6] Kramers[7] has shown that the dipole-dipole interaction
between the two unpaired electron spins, when averaged over
the rotation, removes the degeneracy of the rotational levels
in the observed manner. There is also a weaker Hund's case (b)[6]
coupling of the spin with the total angular momentum apart
from spin, but this term is negligible for our purposes.

Our total Hamiltonian for oxygen in methane includes the
contributions from rotation, crystal field, and spin-spin
interactions.

$$\mathcal{H}_{total} = \mathcal{H}_{rot} + \mathcal{H}_{cryst\ field} + \mathcal{H}_{ss}. \tag{1}$$

The spin-spin coupling arising from the interaction of
the two magnetic-dipole moments is of the form

$$\mathcal{H}_{ss} = \left(\frac{\mu_1 \cdot \mu_2}{|r|^3} - \frac{3(\mu_1 \cdot r)(\mu_2 \cdot r)}{|r|^5} \right) \tag{2}$$

where $|\underset{\sim}{r}|$ is the relative distance between the two dipoles $\underset{\sim}{\mu}_1$ and $\underset{\sim}{\mu}_2$. This spin-spin interaction may be expressed in the form[8]

$$\mathcal{H}_{ss} = A\{(S_z^2 - \frac{1}{4}(S^+S^- + S^-S^+))(3\cos^2\theta - 1)$$

$$+ \frac{3}{2}\sin\theta\cos\theta[(S_zS^+ + S^+S_z)e^{-i\phi} + (S_zS^- + S^-S_z)e^{i\phi}] \qquad (3)$$

$$+ \frac{3}{4}\sin^2\theta[(S^+)^2 e^{-i2\phi} + (S^-)^2 e^{i2\phi}]\}$$

where A is a constant measuring the strength of the interaction. Here the spin-spin Hamiltonian is expressed in terms of the total spin $\underset{\sim}{S} = \underset{\sim}{S}_1 + \underset{\sim}{S}_2$ with $S^\pm = S_x \pm iS_y$ and the polar coordinates refer to the orientation of the vector from spin 1 to spin 2.

The basis $|Km_K m_S\rangle$ proves to be convenient where K is the rotational quantum number and m_K and m_S are the components of K and S on the z-axis, respectively. The kinetic energy yields only the familiar diagonal contributions $B_oK(K+1)$. The spin term $\mathcal{H}_{ss}$ yields non-zero matrix elements only between states where $m_J = m_K + m_S =$ constant. These have been evaluated by others[7,9] and were verified.[5]

If the cubic-crystal-field potential is expressed as an expansion in spherical harmonics, the matrix elements $\langle K'm_K'm_S'|V|Km_Km_S\rangle$ can easily be calculated. The first non-constant set of spherical harmonics $(Y_{\ell m})$ which yield linear combinations totally symmetric (A_1) in an octahedral field are the $\ell = 4$ states. The appropriate linear combination[10] is given by

$$V(\theta,\phi) = XO_h \left(\frac{-2\sqrt{\pi}}{15\sqrt{7}}\right)\left(\sqrt{7}\ Y_{40}(\theta,\phi) + \frac{\sqrt{5}}{\sqrt{2}}\ [Y_{44}(\theta,\phi) + Y_{4-4}(\theta,\phi)]\right) \qquad (4)$$

where XO_h is a measure of the strength of the field.

Devonshire,[11] the first to consider the rotation of diatomic molecules in fields of octahedral symmetry, constructed a potential equivalent to that in Eq. (4). For a positive potential constant there are six equivalent C_{4v} minima and eight equivalent C_{3v} maxima. For a face-centered cubic lattice one would expect less repulsive interaction for an oxygen pointing along the diagonal of the cube. This implies a negative value for the constant XO_h and yields eight equivalent C_{3v} potential minima for an oxygen occupying a methane site.

The crystal field contributions were readily evaluated using the relationship of spherical harmonics

$$\langle \ell'm'|Y_{LM}|\ell m\rangle = (-1)^{-m'} \left[\frac{(2\ell'+1)(2\ell+1)(2L+1)}{4\pi}\right]^{1/2}$$

$$\times \begin{pmatrix} \ell' & L & \ell \\ -m' & M & m \end{pmatrix}\begin{pmatrix} \ell' & L & \ell \\ 0 & 0 & 0 \end{pmatrix} \qquad (5)$$

where the 3-j symbols

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix},$$

have been tabulated by Rotenberg et al.[12] and are also available in computer subroutines. One notes that the crystal field does not affect the spin states. Hence, $\langle K'm_K'm_s'|V|Km_K m_s\rangle$ vanishes unless $m_s' = m_s$.

With the methods described, the Hamiltonian matrix was constructed and diagonalized to obtain the energy eigenvalues and eigenfunctions. The values[6] $B_o = 1.437777$ cm^{-1} and $\lambda = 3/2 \, A = 1.984$ cm^{-1} were used in calculating the energy levels for various values of the potential parameter XO_h. Only odd values of K are allowed for $^{16}O_2$, the dominant isotopic species.

Table I summarizes the resulting energies relative to the ground state. Figure 1 shows the fine structure splitting calculated for oxygen in the gas phase ($XO_h = 0$), and the additional splitting which arises in a weak octahedral field.

The calculations were made using a basis set with a maximum rotational value of K = 7. The 3(2K+1) states for each K value yielded a total of 108 basis functions. This was a sufficiently large basis set to give an accurate description of the behavior of the levels which are populated at low temperatures.

The heat capacity for oxygen in a cubic field was calculated for various values of XO_h, using the usual statistical mechanical equations, and is shown in Fig. 2. In interpreting these results it is useful to note that the maximum difference in potential for molecular rotation is $1/3 \, |XO_h|$. For negative values of this constant the lowest potential barrier between minima is $|XO_h|/12$. Thus an XO_h value of -100 cm^{-1} implies a barrier between minima of 8.3 cm^{-1}.

TABLE I. Energy levels of oxygen in a cubic field for the rotational levels K = 1,3

	Energy (cm^{-1})					
$XO_h(cm^{-1})$ =	10.0	0.0	-10.0	-20.0	-100.0	-500.0
K = 1	0.00(1)*	0.00(1)	0.00(1)	0.00(1)	0.00(1)	0.00(1)
	1.97(2)	2.11(5)	2.02(3)	1.94(3)	1.52(3)	0.75(3)
	2.20(3)		2.24(2)	2.35(2)	2.94(2)	3.50(2)
	3.97(3)	3.97(3)	3.97(3)	3.96(3)	3.88(3)	3.73(3)
K = 3	16.09(1)	16.24(5)	15.94(3)	15.43(3)	11.95(3)	5.50(3)
	16.09(2)		16.19(2)	16.11(2)	16.65(2)	29.16(2)
	16.22(3)	16.43(9)	16.27(3)	16.25(3)	16.97(3)	29.61(3)
	16.26(3)		16.63(3)	16.82(3)	18.21(3)	31.27(3)
	16.54(2)		16.66(2)	17.04(2)	18.91(1)	31.71(1)
	16.76(3)		16.85(1)	17.34(1)	21.77(2)	41.00(1)
	18.34(3)	18.35(7)	18.25(1)	18.20(1)	22.47(1)	41.20(3)
	18.49(1)		18.46(3)	18.69(3)	23.02(3)	41.24(2)
	18.55(3)		18.48(3)	18.83(3)	23.65(3)	41.46(3)

* The degeneracy of each level is denoted in parentheses. The constants B_o = 1.43777 cm^{-1}, λ = 1.984 cm^{-1} were used in the calculation.
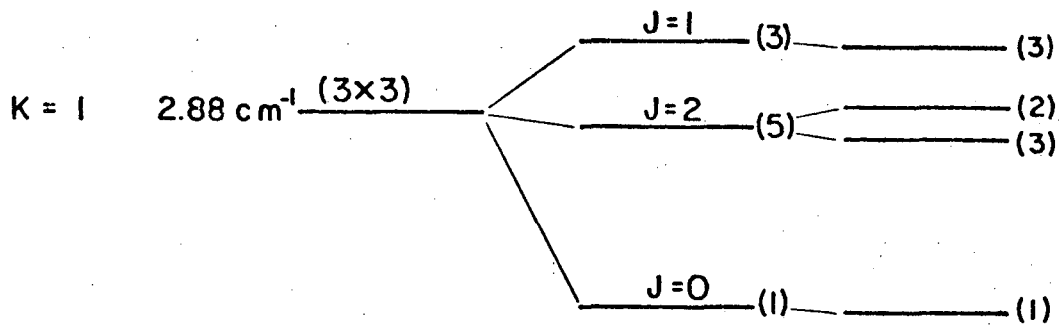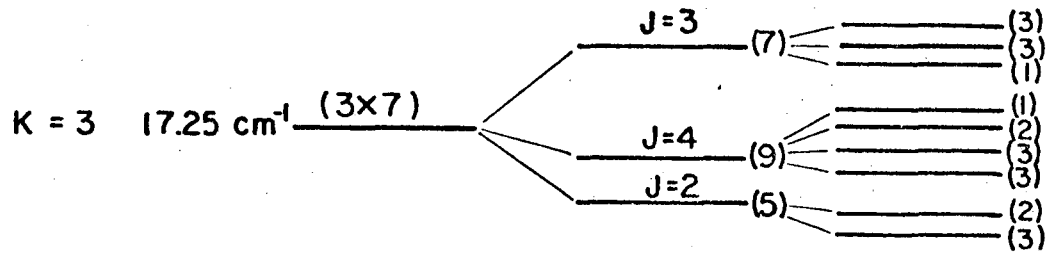
$XO_h = 0$ $XO_h = -10\ cm^{-1}$

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Fig. 1

Also included in Fig. 2 is the heat capacity curve for an infinite potential barrier which represents the case where the molecular rotation is reduced to torsional vibration of small amplitude. This is essentially the situation found for O_2 in lattices of diatomic molecules such as N_2 and CO. Heat capacity measurements by Buford and Graham[13] for these systems show a broad maximum in the oxygen contribution near 2°K with a shape very similar to that shown for ±∞ in Fig. 2. In the diatomic-molecule lattices there is undoubtedly an elongated cavity which yields a single lowest level and a doubly degenerate level at $2\lambda = 3.57$ cm^{-1}. With the infinite cubic field one obtains the same pattern but with degeneracies 4 and 8 for large negative XO_h or 3 and 6 for large positive XO_h corresponding to the number of potential minima for a symmetrical linear molecule. The approach to this pattern can be seen in the column for $XO_h = -500$ cm^{-1} in Table I.

In EPR studies of O_2 in an N_2 matrix at 4.2°K, Simoneau, Harvey, and Graham[14] confirmed an axial substitutional site for O_2. In preliminary experiments with O_2 in a CO lattice, they found results almost identical to those in a N_2 lattice. Samples were also prepared with argon and CD_4 matrices; however, these data "showed no distinctive features and were not amenable to analysis." Hence, Simoneau et al. concluded there was no evidence here of an axial site about the O_2 molecule. This result is consistent with our choice of a cubic field for O_2 in methane, but unfortunately it gives only a vague upper limit to the constant for the cubic field.

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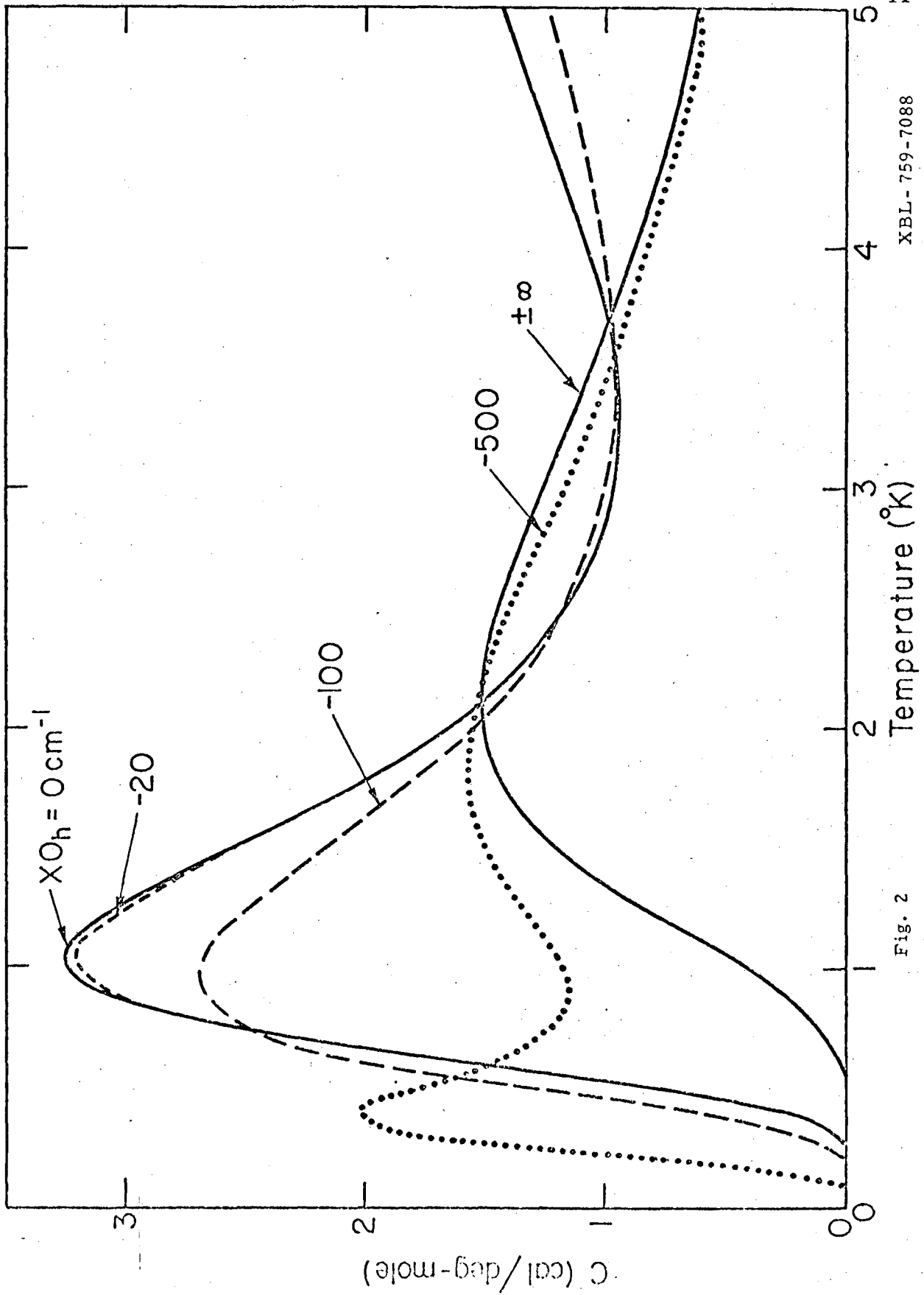
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Fig. 2

While **it** is not possible to set a quantitative value
for the field strength, it is apparent from Fig. 1 that the
heat capacity contribution from a small percentage of oxygen
will not be large and that the value for freely rotating
molecules will set an upper limit near 1°K. Since the peak
observed by Vogt and Pitzer[2f,g] for methane containing 0.8%
O_2 occurs essentially at 1°K, as shown in Fig. 3, their use
of the free-rotation heat capacity for the small contribution
from oxygen seems justified.

In view of the particular interest in this anomaly in
methane near 1°K, we have calculated the population of oxygen
in each of several low-energy states. These results are
given in Table II.
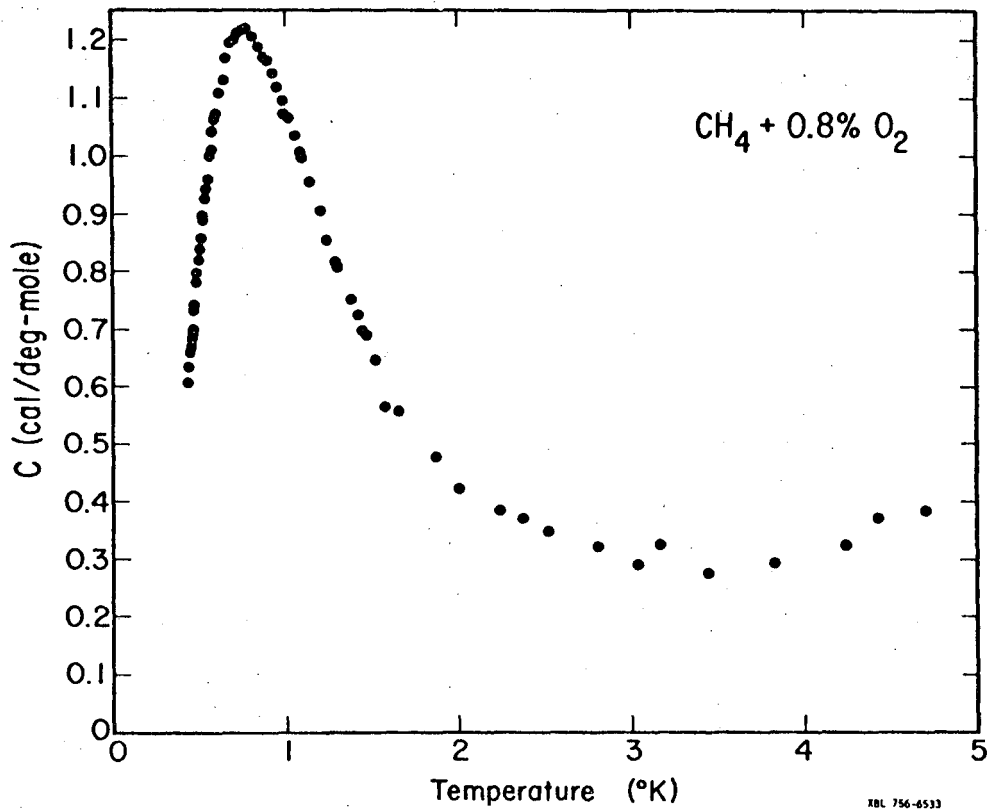
Figure 3.   The heat capacity of methane
catalyzed for spin species conversion.
From Vogt and Pitzer.[2f]

TABLE II. Relative population of the first six levels at
T = 1°K for various field strengths

			$XO_h (cm^{-1})$			
K	J	Degen.	0	-20	-100	-500
1	0	(1)	.800	.793	.726	.488
1	2	(3)	.192	.145	.245	.499
1	2	(2)		.054	.021	.006
1	1	(3)	.008	.008	.008	.007
3	2	(3)	3×10^{-10}	5×10^{-9}	7×10^{-8}	5×10^{-4}
3	2	(2)		1×10^{-10}	6×10^{-11}	6×10^{-19}

III. Mechanism for Oxygen-Catalyzed Spin Conversion in Methane

Bloembergen[15] first considered the theory of nuclear spin relaxation via paramagnetic ion impurities. It was postulated that nuclear spins within a certain radius R_o of the impurity relaxed rapidly via a nuclear-spin-dipole interacting with an impurity electronic spin dipole. Then distant spins are relaxed by spin diffusion. This picture has been refined[16] but not changed basically.

Motizuki and Nagamiya[17] have described the theory of oxygen-induced spin conversion in solid ortho-para hydrogen. The description of oxygen-catalyzed spin conversion in methane is formally the same. However, the interaction with oxygen involves four protons in methane and must be averaged over the more complex rotational motion of methane.

In general the spin change for protons in methane may be induced by an oscillating magnetic field. The unpaired electron spins of oxygen yield an inhomogeneous magnetic field. Oscillations in this field at any given proton can arise from rotation of either the methane or oxygen or oscillation in the distance between them. Since we seek only a qualitative picture of the conversion process we have not investigated all of these aspects. Rather we follow Motizuki and Nagamiya[17] and consider only the rotation of the methane together with the energy requirements including phonons. Presumably the detailed consideration of oxygen rotation and lattice vibration would enhance the rate.

Also the rotation of both oxygen and methane molecules is presumably restricted somewhat in the lattice. A restricted rotational wave function can be expressed in a series where the leading term is the function for free rotation of the appropriate symmetry, etc. While a quantitative evaluation of the rate of conversion would require use of the functions for restricted rotation, the qualitative pattern should be correctly given by use of the leading terms alone and we use this approximation throughout this section.

While our treatment will apply to all states at moderate energy, we have worked out the details only for the low-energy states which are populated near 1°K and are important in spin-species conversion of methane on D_{2d} sites. We will be particularly interested in the catalytic effectiveness of oxygen in the ground state with $J = 0$ since this is a non-degenerate state of zero total angular momentum.

Before considering the nature of the Hamiltonian in detail, a description of the methane molecule is necessary.

A. The Methane Wave Functions

Wilson[18] described the spin statistics for methane using the methods of group theory. The four proton spins couple to yield $2^4 = 16$ possible spin functions for the CH_4 molecule. These 16 wave functions belong to one of the three irreducible representations of the T group. There are five A states which correspond to nuclear spin $I = 2$, three sets of T states ($I = 1$) and one set of E states ($I = 0$). The

rotational wave functions |JKM> of methane are those of a spherical top molecule. Since the product of rotational and spin functions must have symmetry A, only certain spin-species are allowed for a given rotational level.

More detailed definitions of the rotational and spin wave functions for methane have been given by several authors.[19-21] Since we are interested in behavior at very low temperature, we give primary attention to the states with J = 0 and 1 of spin symmetry A and T, respectively.

The rotational function for J = 0 is just $1/2\pi$ and the spin functions are the totally symmetric functions[20] with I = 2 and m_I = 2, 1, 0, -1, and -2 which we write as $|Am_I>$. The product for $\psi(J, m_J, m_I)$ is then

$$\psi(00m_I) = (1/2\pi) |Am_I>. \tag{6}$$

For the nine states with J = 1 and spin symmetry T the situation is more complex. It is convenient to choose both the spin and rotation functions in forms that transform as the Cartesian coordinates in the molecule-fixed frame shown in Fig. 4. The spin functions $|T_x, m_I>$, etc., are given explicitly in Table III.[20]

The rotational wave functions of a spherical-top molecule may be expressed in terms of the normalized D functions[21,22]

$$|JKM> = \psi^{(J)}(\{\alpha\beta\gamma\})_{K,M} = \left[\frac{(2J+1)}{8\pi^2}\right]^{1/2} D^{(J)}[\{\alpha\beta\gamma\}]_{K,M} \tag{7}$$

where the Euler angles $\{\alpha\beta\gamma\}$ describe the molecular orientation with respect to a space-fixed reference axis. We adopt
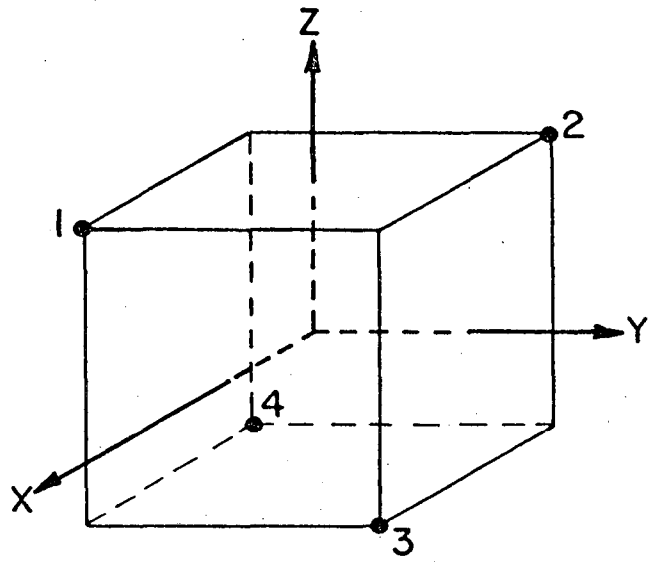
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Fig. 4

TABLE III. The CH_4 spin functions of symmetry T

$$|T_x\ 1> = \frac{1}{2}[(\alpha\alpha\alpha\beta + \alpha\beta\alpha\alpha) - (\alpha\alpha\beta\alpha + \beta\alpha\alpha\alpha)]$$

$$|T_x\ 0> = \frac{1}{\sqrt{2}}(\alpha\beta\alpha\beta - \beta\alpha\beta\alpha)$$

$$|T_x\text{-}1> = \frac{1}{2}[(\alpha\beta\beta\beta + \beta\beta\alpha\beta) - (\beta\alpha\beta\beta + \beta\beta\beta\alpha)]$$

$$|T_y\ 1> = \frac{1}{2}[(\alpha\alpha\alpha\beta + \beta\alpha\alpha\alpha) - (\alpha\alpha\beta\alpha + \alpha\beta\alpha\alpha)]$$

$$|T_y\ 0> = \frac{1}{\sqrt{2}}(\beta\alpha\alpha\beta - \alpha\beta\beta\alpha)$$

$$|T_y\text{-}1> = \frac{1}{2}[(\beta\alpha\beta\beta + \beta\beta\alpha\beta) - (\alpha\beta\beta\beta + \beta\beta\beta\alpha)]$$

$$|T_z\ 1> = \frac{1}{2}[(\alpha\alpha\alpha\beta + \alpha\alpha\beta\alpha) - (\alpha\beta\alpha\alpha + \beta\alpha\alpha\alpha)]$$

$$|T_z\ 0> = \frac{1}{\sqrt{2}}(\alpha\alpha\beta\beta - \beta\beta\alpha\alpha)$$

$$|T_z\text{-}1> = \frac{1}{2}[(\alpha\beta\beta\beta + \beta\alpha\beta\beta) - (\beta\beta\alpha\beta + \beta\beta\beta\alpha)]$$

the convention of Edmonds[23] for defining the D function in Eq. (7).

Yamamoto and Katakoa[21] have shown that the appropriate linear combinations of $|JKM\rangle$ which transform as x, y and z for J = 1 are

$$\psi_{x,M}^{(1)} = \psi_{1,M}^{(1)-} \tag{8a}$$

$$\psi_{y,M}^{(1)} = -i\psi_{1,M}^{(1)+} \tag{8b}$$

$$\psi_{z,M}^{(1)} = \psi_{0,M}^{(1)} \tag{8c}$$

where

$$\psi_{\mu,M}^{(J)\pm} \equiv \frac{1}{\sqrt{2}} \left[\frac{(2J+1)}{8\pi^2} \right]^{1/2} \left[D_{-\mu,M}^{(J)} \pm D_{\mu,M}^{(J)} \right] \tag{9a}$$

$$\psi_{0,M}^{(J)} \equiv \left[\frac{(2J+1)}{8\pi^2} \right]^{1/2} D_{0,M}^{(J)} . \tag{9b}$$

M can take on the values 1, 0, -1, for J = 1, yielding nine rotational wave functions, three sets which transform as either x, y, or z.

The product wave functions, $\psi_{rot}\psi_{spin}$ of J = 1 which are of overall A symmetry would transform as $x^2 + y^2 + z^2$ or for $\psi(J, m_J, m_I)$

$$\psi(1m_J m_I) = 3^{-1/2} (\psi_{x,M}^{(1)} |T_x m_I\rangle + \psi_{y,M}^{(1)} |T_y m_I\rangle$$

$$+ \psi_{z,M}^{(1)} |T_z m_I\rangle) . \tag{10}$$

Since m_J = M and independently m_I may take on values -1, 0, or 1, there are 9 states in all.

B. The Methane-Oxygen Dipole-Dipole Interaction

The interaction between two dipoles has been described in Eq. (2). The magnetic moment μ_1 is that of the oxygen molecule which interacts with the proton spin magnetic moment μ_2 of a CH_4 molecule. The proton magnetic moment μ_2 is proportional to the nuclear spin moment I. While the O_2 magnetic moment has contributions from both the unpaired electron-spin angular momentum and the rotational angular momentum, the dominant term is the electron-spin magnetic moment which is proportional to the electron spin angular momentum S.

The interaction between an O_2 and CH_4 molecule is the sum of the interactions between the oxygen electron-spin and each of the four protons as labeled in Fig. 4.

$$\mathcal{H}(O_2\text{-}CH_4) = \sum_{n=1}^{4} \mathcal{H}(S,I_n). \tag{11}$$

If we recast Eq. (3) in Cartesian coordinates[8,17] we can write the oxygen interaction with the nth proton as

$$\mathcal{H}(S,I_n) = -g_e\beta g_p\beta_N \left\{ [S_z I_{z,n} - \frac{1}{4}(S^+I_n^- + S^-I_n^+)]\left(\frac{R_n^2 - 3Z_n^2}{R_n^5}\right) \right.$$

$$- \frac{3}{2}\left[(S^+I_{z,n}+S_zI_n^+)\frac{(X_n-iY_n)Z_n}{R_n^5} + (S^-I_{z,n}+S_zI_n^-)\frac{(X_n+iY_n)Z_n}{R_n^5}\right]$$

$$\left. - \frac{3}{4}\left[S^+I_n^+\frac{(X_n-iY_n)^2}{R_n^5} + S^-I_n^-\frac{(X_n+iY_n)^2}{R_n^5}\right] \right\} \tag{12}$$

where $g_e \beta \underset{\sim}{S}$ and $g_p \beta_N \underset{\sim}{I}$ are the electron and proton magnetic moments and the coordinates are for the relative distance from the n-th proton to the electron spin centered on the oxygen.

As we proceed to evaluate this expression for the oxygen-methane interaction, let us consider the oxygen transitions which can occur in the process.

C. Spin-Allowed Transition for Oxygen

The allowed oxygen-induced methane transitions are those non-vanishing matrix elements

$$< \psi_i | \mathcal{H}(O_2\text{-}CH_4) | \psi_j > \neq 0. \tag{13}$$

The wave functions for the system are a product of oxygen and methane wave functions

$$\psi_{system} = \psi(O_2) \, \psi_{rot} \, \psi_{spin}(CH_4). \tag{14}$$

The appropriate methane wave functions have been described above. The oxygen wave functions are those obtained from diagonalizing the Hamiltonian for oxygen as discussed in Section II. We now consider only free rotation and give in Table IV the results for $K = 1$, $J = 0, 1$. Note that the complete function is designated by $|J \, m_J>$ whereas the terms on the right are $|m_K m_S>$.

TABLE IV.   Oxygen wave functions for the K=1
            rotational level with J=0 and 1

$|J \ m_J\rangle$	$|m_K m_S\rangle$
$|00\rangle = 3^{-1/2}(-|1-1\rangle + |00\rangle - |-11\rangle)$	
$|11\rangle = 2^{-1/2}(|10\rangle - |01\rangle)$	
$|10\rangle = 2^{-1/2}(|1-1\rangle - |-11\rangle)$	
$|1-1\rangle = 2^{-1/2}(|0-1\rangle - |-10\rangle)$	

Only the spin part of the interaction Hamiltonian
(Eq. 12) will affect the oxygen wave function since we have
assumed oxygen is fixed relative to the rotating methane.
We seek the oxygen "spin-allowed" transitions which are
permitted by the $S(O_2)$ operator where S operates only on
the spin projection m_S.   The S_z, S^+ and S^- operators yield

$$S_z|m_K \ m_S\rangle = m_S \ |m_K m_S\rangle \tag{15a}$$

$$S^+|m_K \ m_S\rangle = [S(S+1) - m_S(m_S+1)]^{1/2} \ |m_K m_S+1\rangle \tag{15b}$$

$$S^-|m_K \ m_S+1\rangle = [S(S+1) - m_S(m_S+1)]^{1/2} \ |m_K m_S\rangle \tag{15c}$$

Thus we find non-vanishing matrix elements for $S^\pm$ if
$\Delta m_S = \pm 1$ and for S_z if $\Delta m_S = 0$ but $m_S \neq 0$.   On substitution
of the wave functions given in Table III, we find that the
following transitions are allowed between the $|00\rangle$ and $|Jm_J\rangle$
states

$$\langle 10|S_z|00\rangle = (2/3)^{1/2}, \qquad \Delta m_S = 0 \qquad\qquad (16a)$$

$$\langle 11|S^+|00\rangle = -2/3^{1/2}, \qquad \Delta m_S = 1 \qquad\qquad (16b)$$

$$\langle 1\text{-}1|S^-|00\rangle = 2/3^{1/2}, \qquad \Delta m_S = -1 \qquad\qquad (16c)$$

Results for some states with higher J are given elsewhere.[5] In general the selection rule for the states of O_2 is $\Delta J = \pm 1$, 0 but with J = 0 to J = 0 forbidden.

For a state with J = 0 the total angular momentum, spin + rotation, add to zero and would seem "spherical". However, the oxygen molecule's coupling with a methane proton is essentially via its electron-spin magnetic dipole which is much stronger than its rotation-induced dipole. The individual components of the J = 0 state, spin and rotation, are not zero, and hence this "weighted" interaction provides a mechanism for catalyzing conversion. Thus the J = 0 ground state may participate in a dipole-dipole interaction inducing methane spin conversions but requires a simultaneous transition to a J = 1 level.

D. Spin-Rotation Transitions for Methane

Our basic assumption that the oxygen molecule was stationary for the time of an oxygen-methane transition allowed us to consider in detail just the spin factor for O_2. This is not possible for methane; rather we must consider in detail both the spin and rotation functions. An appropriate coordinate system is adopted, consistent with Fig. 4, and the corresponding transformations are made for the coordinates

of each of the four protons. The details of this lengthy procedure will not be given here but are outlined in the Appendix and described in greater detail elsewhere.[5] The results are presented in Table V for the allowed transitions between $J = 0$ and $J = 1$ levels of methane.

In Table V the factor arising from the oxygen is given as $\langle S_z \rangle$, $\langle S^+ \rangle$, or $\langle S^- \rangle$ which are abbreviations for the expressions in Eq. (16a, b, c). The factor A arises from the methane functions and is

$$A = 6^{1/2} \, g_e \beta g_p \beta_N \, r/R^4 \tag{17}$$

where r is the C-H distance in methane, 1.1 Å, and R is the distance from the methane to the oxygen molecule.

Our treatment is incomplete in that we have ignored the phonon absorption or emission and the oscillations in R and possibly other coordinates which would be involved. The phonon energies required for these low-level transitions are well within the elastic or acoustic band for solid methane;[24] hence, the transitions will remain allowed, but the quantitative transition probabilities will be affected. Also it is necessary to consider the phonon population at a given temperature when phonons are absorbed.

TABLE **V.** Oxygen-induced transitions for methane
between the J=0 and J=1 levels

Initial State J=0	Final State J=1		Transition Matrix Element
m_I	m_J	m_I	
± 2	0	± 1	$\pm A<S^{\pm}>$
± 2	± 1	± 1	$2^{1/2} A<S_z>$
± 1	0	± 1	$2A<S_z>$
± 1	0	0	$\pm 2^{-1/2} A<S^{\pm}>$
± 1	± 1	± 1	$\mp 2^{-1/2} A<S^{\mp}>$
± 1	± 1	0	$A<S_z>$
± 1	∓ 1	± 1	$\pm 2^{-1/2} A<S^{\pm}>$
0	0	0	$(4/3^{1/2}) A<S_z>$
0	0	± 1	$\mp 6^{-1/2} A<S^{\mp}>$
0	± 1	0	$\mp (2/3)^{1/2} A<S^{\mp}>$
0	± 1	∓ 1	$3^{-1/2} A<S_z>$

IV. Conclusions and Discussion

We are now in a position to consider the actual spin-species transformation in oxygen-doped solid methane at low temperature. The structure of methane below 20.4°K was described in the Introduction. We consider first the methane molecules on D_{2d} sites as the temperature is lowered near 1°K. The important features for CH_4 and O_2 are shown in Fig. 5; a phonon must also be absorbed or emitted to conserve energy. From Table II it is seen that there are appreciable populations of all of the oxygen states arising from K = 1 at 1°K. Thus the methane transition from T to A spin-species (J from 1 to 0) can arise from several different oxygen transitions with appropriate phonon absorption or emission.

As the temperature drops even lower, at about 0.3°K, however, this process would become much slower. Now the oxygen molecules are almost entirely in the J=0 state with only 0.02% in the J=2 states at 2.1 cm^{-1} and only one part in 10^8 in the J=1 states at 4 cm^{-1}. Phonons of these energies are comparably rare. Thus processes starting with oxygen in the J=1 state will become very slow. Processes starting with oxygen in the J=2 state will be slowed less, but the population in this state is only 0.02%. Processes starting with oxygen in the J=0 state require absorption of a phonon of energy 4-1.3 = 2.7 cm^{-1} and the population of such phonons will be small.

While our calculations allow only qualitative conclusions, it is apparent that all of the conversion processes considered
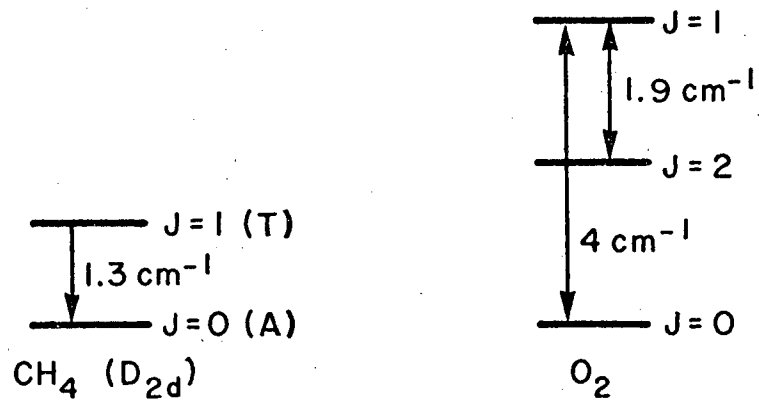
$$J = 1 \ (T)$$
$$\big\downarrow 1.3 \ cm^{-1}$$
$$J = 0 \ (A)$$
$$CH_4 \ (D_{2d})$$

$$J = 1$$
$$1.9 \ cm^{-1}$$
$$J = 2$$
$$4 \ cm^{-1}$$
$$J = 0$$
$$O_2$$

Fig. 5

above will become markedly slower as the temperature decreases below 0.3°K. Thus it seems likely that on a laboratory time scale the spin-species population of methane would be frozen at a level in the range 0.1 to 0.3°K even if cooled further in the presence of oxygen. If conversion continued in this temperature range it would have to be by a mechanism different than the one here considered. Above about 0.3°K, however, a reasonable conversion rate is expected as explained above.

For the molecules on O_h sites the diagram of Fig. 5 is modified by increasing the energy change for methane to about 9 cm^{-1} instead of 1.3. The thermal excitation of these molecules in O_h sites occurs at higher temperatures where the necessary phonon energy will be available. Hence, oxygen catalysis should be effective for the conversion of these molecules.

Our results should be useful in considering other properties of oxygen-doped methane at low temperatures but we will not carry the discussion further.

Acknowledgement

APPENDIX

Spin-Rotation Transitions in Methane

Since the relative distances change as methane rotates
and must be taken into account in the evaluation of the
transition matrix elements, it is more convenient to express
the relative coordinates (X_n, Y_n, Z_n) in terms of the center
of mass coordinates $(0,0,R)$ and the internal coordinates
(x_n, y_n, z_n) which describe CH_4 rotation. For simplicity we
have assumed the center of the CH_4 molecule remains a fixed
distance R apart along the z_{axis} above the oxygen molecule.

If a proton initially positioned at $(x_{n_o}, y_{n_o}, z_{n_o})$ at
Euler angle $(0, 0, 0)$ (Fig. 4) is rotated through the Euler
angles (α, β, γ), the final position of the n-th proton
(x_n, y_n, z_n) can be related to its initial coordinates via
the rotational transformation matrices which describe the
rotation through the angles (α, β, γ). Using Eqs. 7 and 8
we find that the relative coordinates $(X_n \pm iY_n)$ and Z_n may
be expressed in terms of the initial proton coordinates and
the methane rotational wave functions

$$(X_n \pm iY_n) = \mp \frac{4\pi}{\sqrt{3}}\left(x_{n_o} \psi_{x,\pm1} + y_{n_o} \psi_{y,\pm1} + z_{n_o} \psi_{z,\pm1}\right) \qquad (A1)$$

$$Z_n = R + \frac{2\pi\sqrt{2}}{\sqrt{3}}\left(x_{n_o} \psi_{x,o} + y_{n_o} \psi_{y,o} + z_{n_o} \psi_{z,o}\right) \qquad (A2)$$

In addition we assume as a first approximation $R_n = R$ where
it appears in the denominator in Eq. (12).

To evaluate the allowed $A \leftrightarrow T$ spin transition matrix elements, let us look at the allowed transition from a $J=0$ $|A2\rangle$ spin state of CH_4 due to the Hamiltonian term in Eqs. (11, 12)

$$-g_e \beta g_p \beta_N \sum_{n=1}^{4} \left(\frac{R_n^2 - 3Z_n^2}{R_n^5} \right) (S_z I_{z_n} - 1/4 \ (S^- I_n^+ + S^+ I_n^-)) \qquad (A3)$$

Only the I_n^- term allows $|A2\rangle \rightarrow T$ transitions. Using the above expression for Z_n (Eq. A2)

$$Z_n^2 = R^2 + \frac{4\pi\sqrt{2}}{\sqrt{3}} \left(x_{n_o} \psi_{x,o} + y_{n_o} \psi_{y,o} + z_{n_o} \psi_{z,o} \right)$$

$$+ \frac{2\pi\sqrt{2}}{\sqrt{3}}^2 \left(x_{n_o} \psi_{x,o} + y_{n_o} \psi_{y,o} + z_{n_o} \psi_{z,o} \right)^2 \qquad (A4)$$

When this expression is substituted in Eq. (A3) the R^2 term will allow only $A \leftrightarrow A$ transitions. In fact, only the second term will allow a $J=0 \rightarrow J=1$ transition. This may be seen as follows:

Recall that the $J=1$ product functions are of the form given in Eq. (10). In evaluating the matrix element

$$\langle \psi_{rot}(J=1) \ \psi_{spin}(Tm_I) | \ \sum_n \left(x_{n_o} \psi_{x,o} + y_{n_o} \psi_{y,o} + z_{n_o} \psi_{z,o} \right)$$

$$\times I_n^- | \ \psi_{rot}(J=0) \ \psi_{spin} (A2)\rangle$$

as we perform the sum, the spin term $\langle Tm_I | I_n^- | A2 \rangle$ requires that the resultant $m_i = 1$. The orthogonality of the rotational wave functions requires $m_J = 0$. The value of the transition matrix element is $\langle \psi'_{0_2} | S^+ | \psi_{0_2} \rangle (A)$ where A was given in Eq. (17).

The third term in the expansion of z_n^2 will not contribute to a $J=1$ transition. If one expands the third term in Eq. (A4) we find no $A \leftrightarrow T$ contributions are allowed for the $\sum_n x_{n_o}^2 I_n^-$ terms and similarly for the $y_{n_o}^2$ and $z_{n_o}^2$ terms. Using the definitions in Eqs. (7-9) the cross terms ($x_{n_o} y_{n_o}$, $x_{n_o} z_{n_o}$, $y_{n_o} z_{n_o}$) yield integrals of the product of three D functions. Using various properties of the 3-j symbols[23] the cross terms are also seen to vanish.

The other allowed $A \rightarrow T$ transitions (Table V) are evaluated in similar fashion. In fact all of the spin allowed transitions $\langle \psi_{spin}(T) | I_n | \psi_{spin}(A) \rangle$ follow a similar pattern, and any of the allowed methane transitions from a $J=0$ to a $J=1$ rotational level can be readily described in terms of one of three different categories.

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$$D_{KM}^{(J)} \text{ (Wigner)} = <JM|D|JK>$$

$$D_{KM}^{(J)} \text{ (Edmonds)} = <JK|D|JM>.$$

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FIGURE CAPTIONS

Figure 1. The fine structure splitting of oxygen in a
cubic field. Degeneracies are given in
parentheses.

Figure 2. The heat capacity of oxygen in a cubic field.

Figure 3. The heat capacity of methane catalyzed for
spin species conversion. From Vogt and
Pitzer.[2f]

Figure 4. The orientation of a methane molecule reactive
to the molecule-fixed frame. The carbon atom
at the origin is not shown.

Figure 5. Energy levels for molecules in solid methane
with allowed spin conversion processes.

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