

Magnetic Resonance Molecular-Beam Spectra of Methane

C. H. ANDERSON† AND N. F. RAMSEY

Harvard University, Cambridge, Massachusetts

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A detailed analysis of the hyperfine Hamiltonian for the protons in CH_4 is given using group-theoretical techniques, a generalized concept of irreducible tensor operators being introduced. Experimental results using the magnetic resonance molecular-beam technique are given and compared with the theoretical results. The average spin-rotational constant for the protons was found to be $(+)10.40 \pm 0.10$ kc/sec, and the g value of the rotational magnetic moment for the CH_4 molecule was measured to be $(+)0.3133 \pm 0.0002$. Neither sign was measured, but strong arguments are given that the signs in parentheses are the correct ones. The proton in CHD_3 was also investigated to give, with the CH_4 results, the spin-rotational constant for rotations perpendicular to a carbon-hydrogen bond axis as $(+)17.4 \pm 1.6$ kc/sec and for rotations about the axis as $(-)3.6 \mp 3.2$ kc/sec. A measurement of the quadrupole moment of a substituted deuteron was attempted with inconclusive results.

I. INTRODUCTION

THERE have been a number of measurements on the hyperfine interactions of protons in small, simple molecules, in which a variety of techniques were used to suit the molecule and the particular measurement desired. The hydrogen molecule in particular has been very successfully studied using high-resolution magnetic-resonance molecular-beam techniques.¹ The molecules HF ² and LiH ³ have been studied by both electric- and magnetic-resonance molecular-beam techniques, which in general have complemented each other. The electric-resonance beam method has the advantage that with it a beam of molecules can be selected in a particular rotational angular-momentum state. The more complicated molecules, H_2O ⁴ and NH_3 ,⁵ have been studied by maser and other microwave techniques, where the resolution achieved on the rotational transitions is high enough to resolve the small hyperfine terms. The maser and electric molecular-beam resonance methods, however, cannot be used on methane since it lacks an electric dipole moment in its ground electronic and vibrational state. Its small moment of inertia and high vapor pressure at liquid-nitrogen temperatures, however, make this an ideal molecule, second only to H_2 , for study by magnetic-resonance molecular-beam techniques, since a beam of molecules in only a very few rotational states can be produced.

The major hyperfine interactions of the proton are the magnetic dipole-dipole and the spin-rotational. A

substituted deuteron has the quadrupole interaction as well. The analysis of such interactions in NH_3 has been given in some detail,⁶ and it would seem logical that the analysis for CH_4 might closely follow it. However, in the course of this study it was found that certain matrix elements of the energy vanished, and in understanding why, it was discovered that the operators in the Hamiltonian could be rearranged to display the full symmetry of the problem. This simplified the calculations needed for methane and gave a general method for attacking all problems involving a set of symmetrically placed identical nuclei. In particular, it simplifies the work involved in finding the eigenvalues in ammonia over that which has been published, and can be used to reduce such interactions in asymmetrical molecules to one term for each interaction—although neither of these two applications will be discussed here. Posener has also done work on the general problem of hyperfine interactions in polyatomic molecules, using the analysis of NH_3 as his guide.⁷ His work makes a nice complement to the work outlined here.

The paper is divided into four major sections. The first and largest part deals with the analysis and experiments on the CH_4 molecule which lead to a value for the average spin-rotational constant and also to a value for the electrostatic potential at the proton. The second section is on the proton in CD_3H , and gives a determination of the two independent spin-rotational constants of the proton in methane. The third gives a rough value for the quadrupole interaction of a deuteron in methane, and the fourth gives the results of measurements on the rotational magnetic moment of the methane molecule.

II. ANALYSIS OF THE CH_4 SYSTEM

A. The Hamiltonian

Methane is a spherical-top molecule with the four protons occupying the vertices of a tetrahedron and the carbon nucleus at the center. If it is in its ground electronic and vibrational state and is placed in a homo-

† Present address: RCA Laboratories, Princeton, New Jersey.

¹ N. F. Ramsey, *Molecular Beams* (Oxford University Press, London, 1956).

² M. R. Baker, M. Nelson, J. A. Leavitt, and N. F. Ramsey, *Phys. Rev.* **121**, 807 (1961); R. Weiss, *ibid.* **131**, 659 (1963).

³ R. J. Kolenkow, Ph.D. thesis, Harvard University, 1959 (unpublished); L. Wharton, L. P. Gold, and W. Klemperer, *J. Chem. Phys.* **33**, 1255 (1960); T. R. Lawrence, C. H. Anderson, and N. F. Ramsey, *Phys. Rev.* **130**, 1865 (1963).

⁴ E. B. Treacy and Y. Beers, *J. Chem. Phys.* **36**, 1473 (1962); P. Thaddeus, L. C. Krisher, and J. H. N. Loubster, *J. Chem. Phys.* **40**, 257 (1964); P. Thaddeus, L. C. Krisher, and P. Cahill, *J. Chem. Phys.* **41**, 1542 (1964).

⁵ G. R. Gunther-Mohr, R. L. White, A. L. Schawlow, W. E. Good, and D. K. Coles, *Phys. Rev.* **94**, 1184 (1953); J. P. Gordon, *ibid.* **99**, 1253 (1955).

⁶ G. R. Gunther-Mohr, C. H. Townes, and J. H. VanVleck, *Phys. Rev.* **94**, 1191 (1953).

⁷ D. W. Posener, *Australian J. Phys.* **11**, 1 (1958).

geneous external magnetic field, the effective Hamiltonian, ignoring certain small terms, can be written as

$$H = H_I + H_{II} + H_{III} + H_{IV}, \quad (1)$$

where

$$H_I = B\mathbf{J}^2 - D_i\mathbf{J}_i^4 \quad (2)$$

is the energy associated with the rotation of the molecule and consists of the ordinary rotational term plus a term due to centrifugal distortions.⁸ \mathbf{J}_i^4 is a tensor of rank 4 formed from the components of the angular-momentum operator and is a scalar under the tetrahedral point group T_d . This centrifugal term is much larger than the hyperfine interactions, and for this reason, as will be shown later, it simplifies the analysis for the energy levels.

$$H_{II} = -\sum_{s=1}^4 \mathbf{u}_s \cdot \mathbf{H} - \mathbf{u}_J \cdot \mathbf{H} \quad (3)$$

is the interaction of the four proton dipole moments (\mathbf{u}_s), and the rotational magnetic moment (\mathbf{u}_J) with the external magnetic field (\mathbf{H}), ignoring the small shielding of the field at the protons by the electrons. The magnetic field used in the experiments was greater than a kG, making these terms larger than the hyperfine interactions, so that a high-field approximation is used.

$$H_{III} = -\frac{2_p\mu^2}{I_p^2 R^3} \sum_{s<t}^4 \sum_{r=-2}^2 (-1)^r I_r^{st} R_{-r}^{st} \quad (4)$$

is the direct dipole-dipole interactions of the protons with each other and is written here in spherical tensor form.⁹ The \mathbf{I}^{st} are tensors of rank 2 which are formed from the spin vectors \mathbf{I}^s and \mathbf{I}^t , and the \mathbf{R}^{st} are tensors of rank 2 formed from the unit vectors directed from proton s to proton t .

$$H_{IV} = -\sum_{s=1}^4 \mathbf{I}_s \cdot \mathbf{C}_s \cdot \mathbf{J} \quad (5)$$

gives the spin-rotational interaction using the original sign convention.¹ The vectors \mathbf{I}_s are the four proton spin vectors and \mathbf{J} is the orbital-angular-momentum vector. The tensors \mathbf{C}_s are the spin-rotational tensors associated with their respective nuclei. If we use the primed coordinate system I (given in Fig. 1) for the definition of the body coordinates and consider proton 1 which lies on the z' axis of symmetry, then it is evident that the spin-rotational tensor \mathbf{C}_1' has the form

$$\begin{bmatrix} c_\alpha & 0 & 0 \\ 0 & c_\alpha & 0 \\ 0 & 0 & c_\beta \end{bmatrix}, \quad (6)$$

where c_α and c_β are two independent constants, which in principle can be calculated from the electronic wave function of the molecule, but here will be treated as empirical constants to be determined experimentally.

⁸ K. T. Hecht, *J. Mol. Spectr.* **5**, 355 (1960).

⁹ A. R. Edmunds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1957).

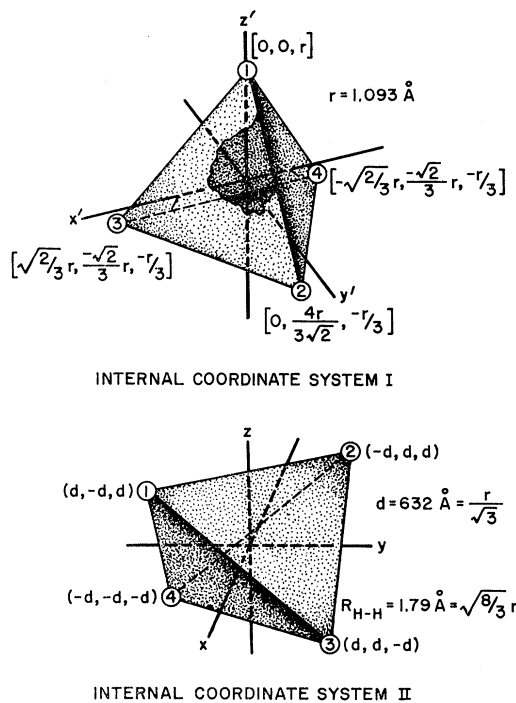


FIG. 1. Molecular coordinate systems for the protons in methane.

Physically, c_α is proportional to the magnetic field per unit of angular momentum generated at a proton by rotations about an axis perpendicular to the carbon-hydrogen bond axis, and c_β is proportional to the magnetic field per unit of angular momentum generated at the proton by rotations about the bond axis.

The unprimed body coordinate system II given in Fig. 1, where the protons occupy alternating octants of the coordinate system, treats all the protons symmetrically and hence is in general a better one to use. Transforming the spin-rotational tensor for proton 1 gives

$$\mathbf{C}_1 = c_a \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} + \frac{1}{3}c_d \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & -1 & 0 \end{bmatrix}, \quad (7)$$

where $c_a = \frac{1}{3}[2c_\alpha + c_\beta]$ and $c_d = c_\alpha - c_\beta$. The other spin-rotational tensors can then be obtained from \mathbf{C}_1 by noticing the symmetries involved to give

$$\mathbf{C}_s = c_a \mathbf{1} + \frac{1}{3}c_d \mathbf{e}_s, \quad (8)$$

where

$$\begin{aligned} \mathbf{e}_1 &= \begin{bmatrix} 0 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & -1 & 0 \end{bmatrix}, & \mathbf{e}_2 &= \begin{bmatrix} 0 & 1 & -1 \\ 1 & 0 & 1 \\ -1 & 1 & 0 \end{bmatrix}, \\ \mathbf{e}_3 &= \begin{bmatrix} 0 & -1 & 1 \\ -1 & 0 & 1 \\ 1 & 1 & 0 \end{bmatrix}, & \mathbf{e}_4 &= \begin{bmatrix} 0 & -1 & -1 \\ -1 & 0 & -1 \\ -1 & -1 & 0 \end{bmatrix}. \end{aligned} \quad (9)$$

Although the hyperfine terms H_{III} and H_{IV} are set down in the usual manner, they do not display all the symmetry of the problem. Before going into this it is

TABLE I. Tetrahedral irreducible representation of the proton spin wave functions $\chi(\gamma, i; I, m_I)$.

$I=2$	m_I	$\chi(A_1, m_I)$
Type A_1	2	$\alpha\alpha\alpha\alpha$
	1	$\frac{1}{2}[\beta\alpha\alpha\alpha + \alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha + \alpha\alpha\alpha\beta]$
	0	$(1/\sqrt{6})[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha + \alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \alpha\beta\alpha\beta + \beta\alpha\beta\alpha]$
	-1	$\frac{1}{2}[\alpha\beta\beta\beta + \beta\alpha\beta\beta + \beta\beta\alpha\beta + \beta\beta\beta\alpha]$
	-2	$\beta\beta\beta\beta$
$I=1$	i	$m_I \chi(F_2, i; m_I)$
	1	$\frac{1}{2}[(\beta\alpha\alpha\alpha - \alpha\alpha\alpha\beta) - (\alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha)]$
	x	0 $(1/\sqrt{2})[\beta\alpha\beta\alpha - \alpha\beta\alpha\beta]$
	-1	$\frac{1}{2}[(\alpha\beta\beta\beta - \beta\beta\beta\alpha) - (\beta\alpha\beta\beta - \beta\beta\alpha\beta)]$
	1	$\frac{1}{2}[(\alpha\beta\alpha\alpha + \alpha\alpha\beta\alpha) - (\beta\alpha\alpha\alpha + \alpha\alpha\alpha\beta)]$
	y	0 $(1/\sqrt{2})[\alpha\beta\beta\alpha - \beta\alpha\beta\beta]$
	-1	$\frac{1}{2}[(\beta\beta\beta\alpha + \alpha\beta\beta\beta) - (\beta\alpha\beta\beta + \beta\beta\alpha\beta)]$
	1	$\frac{1}{2}[(\beta\alpha\alpha\alpha - \alpha\alpha\alpha\beta) + (\alpha\beta\alpha\alpha - \alpha\alpha\beta\alpha)]$
	z	0 $(1/\sqrt{2})[\beta\beta\beta\alpha - \alpha\beta\beta\beta]$
	-1	$\frac{1}{2}[(\alpha\beta\beta\beta - \beta\beta\beta\alpha) + (\beta\alpha\beta\beta - \beta\beta\alpha\beta)]$
$I=0$	i	$\chi(E, i)$
Type E	1	0 $\frac{1}{2}[(\beta\alpha\alpha\beta + \alpha\beta\beta\alpha) - (\beta\beta\alpha\alpha + \alpha\alpha\beta\beta)]$
	2	0 $\frac{1}{2}[(\beta\alpha\alpha\beta + \alpha\beta\beta\alpha) - (\beta\alpha\beta\alpha + \alpha\beta\beta\alpha)]$

useful to present the representation in which the problem will be solved.

B. Wave Functions

The point symmetry group of methane is T_d . It can be shown that the sixteen spin functions for the protons contain the irreducible representations $5A_1 + E + 3F_2$; further it can be shown that the spin functions of symmetry type A_1 correspond to a total spin of 2, those of symmetry type E to a total spin of 0, and those of symmetry type F_2 to a total spin of 1.¹⁰

The wave functions $\chi(\gamma, i; I, m_I)$ are shown explicitly in Table I in terms of the simple product spin functions, where α_s and β_s refer to the spin-up and spin-down states of proton s , respectively. The index γ refers to the symmetry type of the wave function, the index i to a particular function of that symmetry type, I to the total spin, and m_I to the projection of the spin vector on the external z axis.

The F_2 or $I=1$ spin wave functions are exhibited in a form which is isomorphic to the body coordinate axis the in coordinate system II, that is, they transform as components of a vector under the transformations of the point group T_d . To see this, consider the four unit vectors directed toward the protons given by

$$\begin{aligned} \mathbf{r}_1 &= (1/\sqrt{3})[1, -1, 1], & \mathbf{r}_3 &= (1/\sqrt{3})[1, 1, -1], \\ \mathbf{r}_2 &= (1/\sqrt{3})[-1, 1, 1], & \mathbf{r}_4 &= (1/\sqrt{3})[-1, -1, -1]. \end{aligned} \quad (10)$$

From these we can construct the four vectors

$$\begin{aligned} \mathbf{r}_{A_1} &= \frac{1}{2} \sum \mathbf{r}_s = [0, 0, 0], \\ \mathbf{r}_x^{F_2} &= \frac{1}{2}[\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}_3 - \mathbf{r}_4] = (2/\sqrt{3})[1, 0, 0], \\ \mathbf{r}_y^{F_2} &= \frac{1}{2}[-\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3 - \mathbf{r}_4] = (2/\sqrt{3})[0, 1, 0], \\ \mathbf{r}_z^{F_2} &= \frac{1}{2}[\mathbf{r}_1 + \mathbf{r}_2 - \mathbf{r}_3 - \mathbf{r}_4] = (2/\sqrt{3})[0, 0, 1], \end{aligned} \quad (11)$$

which form the obvious irreducible representation of the group—as shown.

¹⁰ E. B. Wilson, J. Chem. Phys. 3, 276 (1935).

TABLE II. Irreducible representations of the rotational and ground vibrational wave functions of methane.

J	Irreducible representations
0	$A_1 + A_2$
1	$F_1 + F_2$
2	$2E + F_1 + F_2$
3	$A_1 + A_2 + 2F_1 + 2F_2$
4	$A_1 + A_2 + 2E + 2F_1 + 2F_2$
5	$2E + 3F_1 + 3F_2$

Now we note that the original vectors \mathbf{r}_s transform isomorphically to the spin functions $\alpha\beta\beta\beta$, $\beta\alpha\beta\beta$, $\beta\beta\alpha\beta$, $\beta\beta\beta\alpha$, since both sets depend only on a single nuclear coordinate in a one-to-one fashion. Hence if we make the same transformation on these spin wave functions as was made on the vectors \mathbf{r}_s , we obtain the irreducible representation for the $m_I = -1$ wave functions as given in the table. The wave functions for the other values of m_I are then found by successive operations of the ladder operator \mathbf{I}^\pm .

It is instructive to look a little more into the form of these spin functions $\chi(\gamma, i; I, m_I)$. These wave functions form an irreducible representation of the laboratory system, which is assumed to have spherical symmetry, as well as an irreducible representation of the molecular point group. The laboratory system is described by the usual I, m_I representation and the point group by the exactly analogous quantities γ, i . However, in this problem there is the physical restriction that for $\gamma = A_1$, $I = 2$; for $\gamma = E$, $I = 0$; and for $\gamma = F_2$, $I = 1$; and no other γ 's and I 's exist.

In a similar fashion one can give the rotational wave functions of the molecule in the form $\phi(\gamma, i; J, m_J, \mathcal{p})$, where γ and i have the meaning given above, J and m_J are the angular momentum and its magnetic quantum numbers, respectively, and \mathcal{p} refers to any additional multiplicities not taken care of by the other quantities. These functions have been constructed explicitly from the symmetric top wave functions $|JKm_J\rangle$ by Jahn for J 's up to 10.¹¹ The irreducible point representations for each J state are given in Table II up to $J=5$.

The total wave function Ψ is formed out of sums of products of the spin wave functions $\chi(\gamma, i; I, m_I)$ and $\phi(\gamma, j; J, m_J)$. The symmetry of this wave function is restricted by the Pauli exclusion principle to go into minus itself for an odd permutation of the protons; thus

TABLE III. Irreducible representations of $D^\alpha \times D^\beta$ and $[D^\alpha]^\beta$.

$\alpha \backslash \beta$	A_1	A_2	E	F_1	F_2
A_1	A_1	A_2	E	F_1	F_2
A_2	A_2	A_1	E	F_2	F_1
E	E	E	$\mathbf{E} + A_1 + A_2$	$F_1 + F_2$	$F_1 + F_2$
F_1	F_1	F_2	$F_1 + F_2$	$A_1 + \mathbf{E} + F_1 + F_2$	$A_2 + E + F_1 + F_2$
F_2	F_2	F_1	$F_1 + F_2$	$A_2 + E + F_1 + F_2$	$A_1 + \mathbf{E} + F_1 + F_2$

¹¹ H. M. Jahn, Proc. Roy. Soc. (London) A168, 469 (1938).

Ψ must be of symmetry type A_2 . Hence if the spin function is of symmetry type α and the orbital wave function is of symmetry type β , we must have the open product $D^\alpha \times D^\beta$ contain D^{A_2} .

Using the reduction of the open products of the irreducible representations with themselves as given in Table III, the acceptable total wave functions are given by the forms

$$\begin{aligned} \Psi(J, m_J; I=2, m_I; \rho) &= \chi(A_1; m_I) \phi(A_2; J, m_J; \rho), \\ \Psi(J, m_J; I=1, m_I; \rho) &= \sum_{i,j}^3 b_{ij} \chi(F_2, i; m_I) \phi(F_1, j; J, m_J; \rho), \quad (12) \\ \Psi(J, m_J; I=0; \rho) &= \sum_{i,j}^2 a_{ij} \chi(E, i) \phi(E, j; J, m_J; \rho). \end{aligned}$$

Because the F_2 spin functions and F_1 orbital wave functions can be defined to transform as polar and axial vectors respectively, the second form is simply a dot product and so $b_{ij} = (1/\sqrt{3})\delta_{ij}$. Similarly the E wave functions can be assumed to be defined such that $a_{ij} = (1/\sqrt{2})\delta_{ij}$ with no loss in generality.

The states allowed for each J value are those of A_2 , E , and F_1 symmetry as given in Table II.

C. Symmetrization of the Hyperfine Operators

A general term in the hyperfine Hamiltonian has the form $\mathbf{h} = \sum_s \mathbf{g}_s \mathbf{f}_s$, where the \mathbf{f}_s operate on the rotational part of the wave function, the \mathbf{g}_s on the spin part, the sum is over all the proton sites or pairs of sites and even possibly larger groupings, and the nature of the products will be clarified below. The symmetry of \mathbf{h} has to be A_1 (i.e., a scalar) since the energy can never be changed by any of the transformations which bring the molecule into itself. The operators \mathbf{f}_s and \mathbf{g}_s , on the other hand, can change into one another under an element of the group and thus form representations of the group which are usually reducible. By taking certain linear combinations of the \mathbf{f}_s we can form an irreducible representation of the group. Call this representation for the \mathbf{f} operators \mathbf{f}_t^γ , where t denotes a member of the set of operators of symmetry type γ . Then define a set of operators \mathbf{g}_t^γ which transform contragradiently to the \mathbf{f}_t^γ , so that the total operator can be rewritten in the form

$$\mathbf{h} = \sum_\gamma \sum_t \mathbf{f}_t^\gamma \mathbf{g}_t^\gamma. \quad (13)$$

This process is exactly identical to the usual one of putting operators into the irreducible representation of the space or laboratory system with spherical symmetry as was done, for example, with the magnetic dipole-dipole interaction in the first section. Usually the

operators \mathbf{f} and \mathbf{g} are also spherical tensors of some rank with components f_q^l ($q = -l \cdots l$) and the interaction takes on the form $\sum (-1)^q f_q^l g_{-q}^l$ to make it a scalar under rotations in the laboratory coordinates.

Now we see that this concept can be generalized so that the quantities $f_{tq}^{\gamma l}$ form the components of a tensor operation of symmetry γ in the point group of the molecular coordinate system and of symmetry l in the continuous spherical group of the laboratory system, and to form a scalar in both coordinate systems a dot product has to be performed in both systems as given by

$$\mathbf{f}^{\gamma l} : \mathbf{g}^{\gamma l} \equiv \sum_t \sum_q (-1)^q f_{tq}^{\gamma l} g_{t,-q}^{\gamma l}. \quad (14)$$

This concept of putting the operators into an irreducible representation of both the laboratory and molecular coordinate systems seems to have been missed in the past, although it has been used in the construction of the wave functions. In fact, it must be possible to apply this technique to any quantity which is a function of both laboratory and internal coordinates.

D. Selection Rules

The procedure of symmetrizing the operators has the advantage of simplifying the calculation of matrix elements. Consider the general matrix element

$$\begin{aligned} \Psi^*(J', m_{J'}; I', m_{I'}; \rho') \mathbf{f}^{\gamma l} : \mathbf{g}^{\gamma l} \Psi(J, m_J; I, m_I; \rho) \\ = \sum_{t,q} (-1)^q \sum_{i,j} \phi^*(\alpha', i; J', m_{J'}; \rho') \\ \times f_{tq}^{\gamma l} \phi(\alpha, j; J, m_J; \rho) \chi^*(\beta', i; I', m_{I'}) g_{t,-q}^{\gamma l} \\ \times \chi(\beta, j; I, m_I). \quad (15) \end{aligned}$$

The theorem on selection rules states that all matrix elements of the form $\Psi^*(\alpha, i) O_q^\gamma \chi(\beta, j)$ are nonvanishing only if the open product $D^\alpha \times D^\beta \times D^\gamma$ includes the unit representation, or what is the same thing, if $D^\alpha \times D^\beta$ includes D^γ . And in the case of diagonal matrix elements the condition becomes the more stringent one of requiring D^γ to be included in the symmetric subgroup $[D^\alpha]_2^2$ of $D^\alpha \times D^\alpha$. Thus the above general matrix element will vanish unless the following are all *simultaneously* satisfied:

$$\begin{aligned} \text{(i)} \quad D^{J'} \times D^J \supset D^I, & \quad \text{(iii)} \quad D^{\alpha'} \times D^\alpha \supset D^\gamma, \\ \text{(ii)} \quad D^{I'} \times D^I \supset D^I, & \quad \text{(iv)} \quad D^\beta \times D^\beta \supset D^\gamma, \end{aligned} \quad (16)$$

where the first two are the more familiar vector addition rules of the spherical group and the second two are the equivalent statements in the molecular point group. Note also that the way the spherical tensors are constructed, we have the conditions $m_{J'} + q = m_J$ and $m_{I'} - q = m_I$. If the point-group components are also carefully constructed, similar rules can be made to apply, as well as all the other concepts of reduced matrix elements.

E. Evaluation of the Matrix Elements of the CH₄ Hamiltonian

We can now go ahead and evaluate the matrix elements of the Hamiltonian and obtain the energy levels to first order for the $I=2$ and $I=0$ states. To do this we first note that in methane the total spin state of the protons determines the symmetry type of the spin wave functions and, through the Pauli exclusion principle, the symmetry type of the orbital wave functions. Hence only one of the above conditions need be considered. Also, reference will be made to the reduction of the open products given in Table III.

The rotational energy term $H_I = B\mathbf{J}^2 - D\mathbf{J}_I^4$ is a simple operator of symmetry type A_1 and thus has nonvanishing matrix elements only if $D^\alpha \times D^{\alpha'} \supset D^{A_1}$, which gives $\alpha = \alpha'$. This is an obvious statement, since the operator is diagonal in the total spin I and thus is diagonal in all the related symmetry quantum numbers. If it were not for the centrifugal distortion term, all the energy levels for a given J would be degenerate and so could easily be mixed by the hyperfine terms. But the centrifugal-distortion splittings, calculated by Hecht up to $J=12$, are much larger than H_{III} and H_{IV} , so that the symmetry quantum numbers (as well as the total spin) are very good and a first-order perturbation calculation on the hyperfine terms can be carried out.

The factors in $H_{II} = -\sum_{s=1}^4 \mathbf{u}_s \cdot \mathbf{H} - \mathbf{u}_J \cdot \mathbf{H}$ can be rewritten as

$$-g_p \mu_N H I_z - g_J \mu_N H J_z, \quad (17)$$

where g_p = the nuclear g factor of the proton, g_J = the rotational g factor, μ_N = a nuclear magneton, H = the magnitude of the external field, $I_z = \sum_{s=1}^4 I_z^s$ = the spatial z component of the total spin, J_z = the spatial z component of the molecular angular momentum. Again these are simple A_1 operators which are diagonal in the representation given in Sec. IIB with eigenvalues

$$-g_p \mu_N H m_I - g_J \mu_N H m_J. \quad (18)$$

The magnetic field used in this problem was around 1600 G, so that this term was also much larger than the hyperfine terms H_{III} and H_{IV} . This also makes m_I and m_J good quantum numbers to first order.

The spin-rotational interaction

$$H_{IV} = -\hbar \sum_{s=1}^4 \mathbf{I}^s \cdot \mathbf{C}_s \cdot \mathbf{J}$$

is a good example of one of the general operators in the last section, although it usually is not convenient to put it into irreducible spherical-tensor form. Before evaluating matrix elements we first have to put the quantities \mathbf{I}_s and \mathbf{C}_s into their irreducible forms of the point group. This is done very easily by noting that they both transform isomorphically to the vectors \mathbf{r}_s considered in

Sec. IIB. Thus we have

$$\begin{aligned} \mathbf{I}^{A_1} &= \mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3 + \mathbf{I}_4 = \mathbf{I}, \\ \mathbf{I}_x^{F_2} &= \mathbf{I}_1 - \mathbf{I}_2 + \mathbf{I}_3 - \mathbf{I}_4, \\ \mathbf{I}_y^{F_2} &= -\mathbf{I}_1 + \mathbf{I}_2 + \mathbf{I}_3 - \mathbf{I}_4, \\ \mathbf{I}_z^{F_2} &= \mathbf{I}_1 + \mathbf{I}_2 - \mathbf{I}_3 - \mathbf{I}_4, \end{aligned} \quad (19)$$

where x, y, z refer to the molecular point-group transformation properties of these vectors and not to a particular spatial component of the vectors.

Similarly we have

$$\begin{aligned} \mathbf{C}^{A_1} &= \frac{1}{4} \sum_{s=1}^4 \mathbf{C}_s = c_a \mathbf{I}, \\ \mathbf{C}_x^{F_2} &= \frac{1}{3} c_d \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} = \frac{1}{3} c_d \mathbf{e}_x^{F_2}, \\ \mathbf{C}_y^{F_2} &= \frac{1}{3} c_d \begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} = \frac{1}{3} c_d \mathbf{e}_y^{F_2}, \\ \mathbf{C}_z^{F_2} &= \frac{1}{3} c_d \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} = \frac{1}{3} c_d \mathbf{e}_z^{F_2}. \end{aligned} \quad (20)$$

Thus we can rewrite H_{IV} in the form

$$-hc_d \mathbf{I} \cdot \mathbf{J} - \frac{1}{3} hc_d \sum_{i=x,y,z} \mathbf{I}_i^{F_2} \cdot \mathbf{e}_i^{F_2} \cdot \mathbf{J}. \quad (21)$$

The diagonal matrix elements of the first term can now be evaluated in a conventional manner, since it is at an operator of symmetry type A_1 , to give

$$-hc_d m_I m_J. \quad (22)$$

The second term can have nonvanishing diagonal matrix elements only if $[D^\alpha]^2 \supset D^{F_2}$, and an inspection of Table III shows that this is true only for $\alpha = E, F_1$, and F_2 . Hence this operator makes no contribution to the diagonal matrix elements of the $I=2$ or symmetry-type- A_1 spin states, but it does have nonvanishing diagonal matrix elements with the $I=1$ or symmetry-type- F_2 spin states. The $I=0$ or E states need not be considered, since all diagonal matrix elements of operators involving the proton spins must vanish for these states.

Note that this operator can have nonvanishing matrix elements between states of different symmetry, and thus would mix them if it were not for the centrifugal-distortion term preventing it.

Finally consider the direct dipole-dipole interaction term given by

$$H_{III} = -\frac{2\mu_p^2}{I_p^2 R^3} \sum_{s < t}^4 \sum_{r=-2}^2 (-1)^r I_r^{st} R_{-r}^{st}. \quad (23)$$

The irreducible forms for the operators I^{st} and R^{st} are again easily formed by noting they transform isomorphically to the spin wave functions for $m_I=0$ (i.e., $\alpha\alpha\beta\beta$, $\alpha\beta\alpha\beta$, $\alpha\beta\beta\alpha$, etc.). Hence, their reduction contains the symmetries A_1+E+F_1 , as shown in Table II for these wave functions. Consider, however, the tensor \mathbf{R}^{A_1} which is associated with the Cartesian tensor $R_{ij}^{A_1}$ in the body coordinates. This must be a tensor completely symmetric under all elements of T_d and yet have a vanishing trace, since it is formed from a sum of traceless tensors (R_{ij}^{st}). The only tensor which satisfies these two conditions simultaneously is the null tensor. Another way to see that this tensor must vanish is to note that it must transform isomorphically to an orbital-angular-momentum wave function for $J=2$, since it is a tensor of rank 2. An inspection of Table II shows that no wave function for $J=2$ has A_1 symmetry and hence \mathbf{R}^{A_1} must vanish. Thus H_{III} can be rewritten as

$$H_{III} = -\frac{2\mu_p^2}{I_p^2 R^3} \left[\sum_{i=1}^2 \sum_{p=-2}^2 (-1)^p I_{ip}^E R_{i-p}^E + \sum_{i=x,y,z} \sum_{p=-2}^2 (-1)^p I_{ip}^{F_2} R_{i-p}^{F_2} \right]. \quad (24)$$

We now see that this term must vanish for the $I=2$ state, since it does not contain any operators of A_1 symmetry. The diagonal matrix elements for the $I=0$ states also vanish, so this term makes a contribution only to the $I=1$ states.

Thus, for the $I=2$ spin states, leaving out the rotational energy terms, we have the eigenvalues

$$W(J, m_J; I=2, m_I) = -\mu_N g_J H m_J - \mu_N g_p H m_I - h c_a m_I m_J. \quad (25)$$

Similarly for the $I=0$ states we have the eigenvalues $W(J, m_J, I=0) = -\mu_N g_J H m_J$.

The spin-1 energy levels are quite complicated to calculate, since the contributions from the F_1 spin-rotational interaction term and the direct dipole-dipole terms require explicit forms for the rotational wave functions. Since these levels have not been clearly resolved in the experiments, they have not been calculated. However, the fact has been used that the dipole-dipole interaction depends on m_I^2 and so these levels are not equally spaced in m_I .

F. Transition Probabilities

The resonances of the total-spin-1 and -2 molecules for a $\Delta m_I = \pm 1$ transition are centered at the Larmor frequency of the protons in the external field and in general overlap one another. The apparatus used in the experiments did not have the resolution to clearly resolve all the lines, and so a condition was found which enhanced the spin-2 lines over the spin-1 lines, thus enabling the simpler spectrum to be observed.

For equally spaced levels, the Majorana formula gives the probability of going from level m to m' under the influence of an oscillating magnetic field at the resonance frequency. If we detect all changes in m with equal sensitivity then all we need is the probability of leaving m . From Ramsey,¹ we have for the probability of staying in level m , for weak rf fields, approximately

$$P_{mm} \cong 1 - 2[I(I+1) - m_I^2] \sin^2(\frac{1}{2}\alpha), \quad (26)$$

where $(\sin^2(\frac{1}{2}\alpha)) =$ the transition probability of a spin- $\frac{1}{2}$ particle to flip under the influence of the rf field. The total resonance signal for a spin state I is then proportional to

$$\sum_{m_I=-I}^I (1 - p_{m_I m_I}) = \frac{4}{3} I(I+1)(2I+1) \sin^2(\frac{1}{2}\alpha). \quad (27)$$

The ratio of the $I=2$ lines to the $I=1$ lines at low rf power levels is 5 if both can undergo multiple transitions. The $I=1$ lines, however, are unequally spaced because of the dipole-dipole interaction, which makes this ratio even larger. Thus low rf levels enhance the spin-2 resonance signal about an order of magnitude over the spin-1 resonance signals.

The resonance frequencies for the spin-2 state are given by $\nu = \nu_p + c_a m_J$, where ν_p is the Larmor frequency of the protons. At liquid-nitrogen temperatures, only a few J states in methane are populated, and so the intensity of the signal for each value of m_J is given approximately by

$$s(\nu_p + c_a m_J) \cong \sum_{J=|m_J|}^5 n(I=2, J) \exp\left[-\frac{BJ^2}{kT}\right], \quad (28)$$

where $n(I=2, J)$ is the number of times the irreducible representation A_2 is given for that J value. An inspection of Table II shows that this quantity is 1 for $J=0, 3, 4$ and 0 for $J=1, 2, 5$. The most striking feature of this spectrum is that the intensities of the resonances for $m_J=1, 2$, and 3 are all equal.

G. The Experiments at 78°K

The experiments with methane have few features different from those carried out previously on the new molecular-beam apparatus at Harvard.^{2,12} Methane was introduced into the source chamber, which was cooled to 78°K by liquid nitrogen, at a pressure of a few mm of mercury and flowed out through a pair of slits 1 mil wide. The molecules were collimated into a beam by a 2-mil slit in the center of the homogeneous \mathbf{C} magnet and were ionized after passing through the detector slits by an electron beam. The ions formed were passed into a mass spectrometer and then focused onto the first dynode of an electron multiplier. The output from the multiplier was then sent into a lock-in amplifier whose output was put into a recorder.

¹² (a) J. A. Leavitt, M. R. Baker, H. M. Nelson, and N. F. Ramsey, Phys. Rev. **124**, 1482 (1961); (b) H. M. Nelson, J. A. Leavitt, M. R. Baker, and N. F. Ramsey, *ibid.* **122**, 856 (1961).

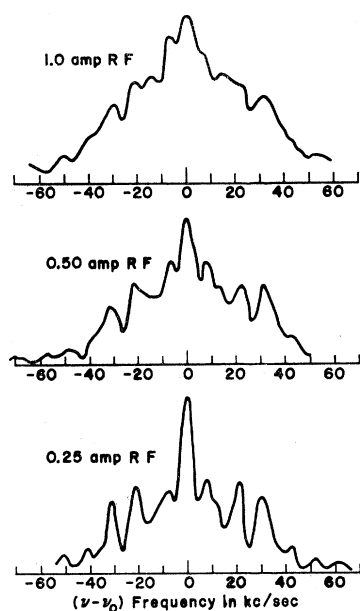


FIG. 2. Proton magnetic resonance spectrum in methane at 78°K and various rf levels.

The beam of methane was detected at all the ion fragments CH_n^+ for $n=0$ to 4. The best signal-to-noise ratio was found using the CH_3^+ ion at mass 15. The ion CH_4^+ at mass 16 had oxygen background problems and the other ions were produced in smaller quantities.

The rf coil in the center of the homogeneous **C** magnet had 3 turns on it and was 3 in long. The **C** field was usually run around 1600 G and so the resonance frequency of the proton was about 7 Mc/sec. The optimum rf current (modulated on-off at 17 cycles) for the proton in HD at 78°K was found to be about 3 A and produced a resolution of about 11 kc/sec in this molecule. Since the heavier methane molecules move slower at 78°K, the optimum rf for a single proton in CH_4 should be around 1.3 A and the resolution should be about 5 kc/sec.

Figure 2 shows the resonance curves for the proton at rf currents of 0.25, 0.50, and 1.0 A, respectively. It is clear that the spectrum becomes unresolved and more complicated at higher rf levels where the $I=1$ lines become more important, as was predicted in the last section. Figure 3 shows half the resonance curve taken at 0.20 A compared with the theoretical calculation for the $I=2$ lines at 78°K, where $|c_a|$ was taken around 10.4 kc/sec.

A detailed analysis of several curves taken with rf currents of 0.20 to 0.50 A has given the consistent value for $|c_a|$ of 10.40 ± 0.10 kc/sec.

H. Statistical Model

When the proton spectrum in CH_4 is studied at room temperature with a short rf coil, a single broad resonance is observed. This curve can be described by the following statistical model.

Let dN , the number of molecules in the state J and

m_J in the range $dJdm_J$, equal

$$A(2J+1) \exp[-BJ^2/kT] dJdm_J. \quad (29)$$

The factor $A(2J+1)$ gives the multiplicity of the possible states of a given J and m_J for a spherical-top molecule. Ignoring spin statistics and the restrictions of the Pauli principle, this factor is simply $2J+1$.

The direct dipole-dipole interaction and the tensor part of the spin-rotational interaction act only on the $I=1$ state and will not shift the average position of the resonance lines of this state from the value $\nu = \nu_p + c_a m_J$; hence we shall assume that this is the only dependence ν has on the quantum numbers.¹³

Making a formal change in variable from m_J to ν in Eq. (26) and integrating over the allowed J values, we have the Gaussian line shape

$$\frac{dN}{d\nu} \cong I_0 \exp\left[-\frac{B}{kT} \left(\frac{\nu - \nu_p}{c_a}\right)^2\right] \quad (30)$$

instead of the error function which is obtained in the linear-molecular case.¹⁴

Figure 4 shows a comparison between an experimental curve taken at room temperature with a $\frac{3}{4}$ in. rf coil, and a theoretical curve for $|c_a| = 10.5$ kc/sec and an

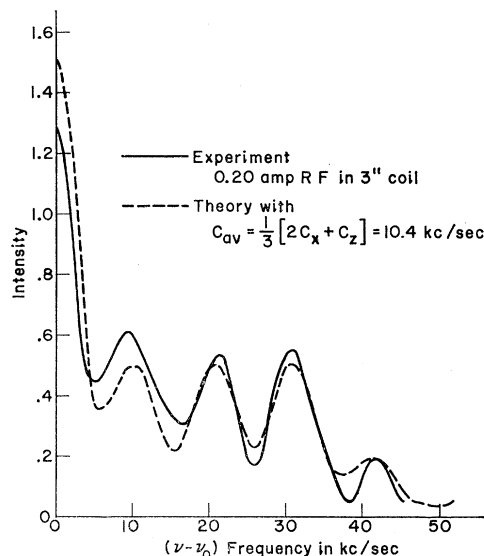


FIG. 3. Comparison between a theoretical and experimental curve for the proton resonance in methane with the beam source chamber at 78°K and rf current about a factor of 5 below optimum to enhance the $I=2$ transitions.

¹³ R. G. Gordon [J. Chem. Phys. 44, 1184 (1966)], in analyzing the room-temperature CH_4 data of this work, included the tensor part of the spin-rotational interaction and then concluded that the interaction constant c_d is small, in contradiction to the results discussed in Sec. IV. The identity of the four protons in CH_4 , which was not properly taken into account in Gordon's calculation, leads to an averaging of the c 's among the different protons and to a consequent diminution of the apparent value of c_d , so the limits he set for c_d are excessively narrow.

¹⁴ W. A. Nierenberg and N. F. Ramsey, Phys. Rev. 72, 1075 (1947).

intrinsic line width of 25 kc/sec. The close agreement is better than one would expect, since only J up to about 12 are excited, and in fact the disagreement near the origin must be due to the low- J states, which make a major contribution in this region.

Fitting the experimental curve with the theory gave the value for $|c_a|$ of 10.5 ± 0.3 kc/sec, which is in very good agreement with the resolved structure. This makes applications of this statistical model to other spherical-top molecules appear somewhat more reliable.

A better molecule to apply such a statistical model to is CF_4 , which has a most probable J of about 27 at room temperature. The fluorine resonance was run in this molecule at room temperature and produced an almost perfect Gaussian with a full width at half-height of 356 kc/sec. Analysis of this curve gave a value of 5.8 ± 1.0 kc/sec for $|c_a^{\text{F}}|$ of the fluorine nuclei in CF_4 .

III. DETERMINATION OF THE SIGN OF c_a IN CH_4

Ramsey's relationship between the spin-rotational interaction and the shielding constant¹⁵ was generalized to polyatomic molecules by Schwartz.¹⁶ One of the more convenient ways to express this relationship is¹⁷

$$\sigma_n = \frac{-V_n}{3m_e c^2} + \frac{2\pi m_p}{g_n m_e \hbar^3} \text{Tr} \mathbf{C}_n \cdot \mathbf{I}_n, \quad (31)$$

where

- σ_n = the shielding constant for the nucleus n .
- $V_n = e^2 \int (\rho_n/r_n) d\tau$ = the electrostatic potential energy at the nucleus n .
- ρ_n = the total charge distribution in the molecule except for the nucleus n .
- \mathbf{C}_n = the spin rotational tensor for the nucleus n .
- g_n = the nuclear "g" factor for the nucleus n .
- \mathbf{I}_n = the moment of inertia tensor for the molecule.
- m_p = the mass of the proton.
- m_e = the mass of the electron.

and

$$c = \text{the velocity of light.}$$

This expression ignores corrections for zero-point vibrations and the Thomas precession, both of which should be less than a few percent, and hence usually less than the experimental errors involved.

If we assume that V_n for a given nucleus does not change appreciably from one molecule to another, the chemical shift can be related to the spin-rotational constants as

$$\delta = \sigma_n^{(1)} - \sigma_n^{(2)} \cong \frac{2\pi m_p}{g_n m_e \hbar^3} [\text{Tr} \mathbf{C}_n^1 \mathbf{I}_n^1 - \text{Tr} \mathbf{C}_n^2 \mathbf{I}_n^2]. \quad (32)$$

¹⁵ N. F. Ramsey, Phys. Rev. **78**, 699 (1950).

¹⁶ R. Schwartz, Ph.D. thesis, Harvard University, 1952 (unpublished).

¹⁷ J. Pinkerton, Ph.D. thesis, Harvard University, 1961 (unpublished); C. H. Anderson, Ph.D. thesis, Harvard University, 1961 (unpublished).

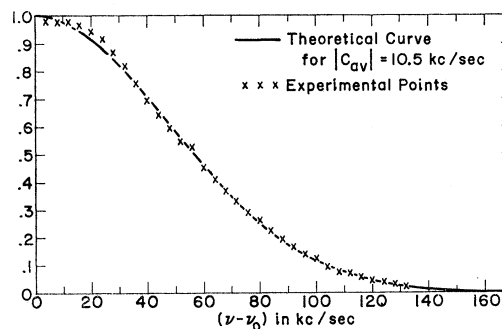


FIG. 4. Experimental and statistical-model curves for the proton in methane with the source temperature at 300°K.

Using the chemical shift of 4.20 ppm between H_2 and CH_4 ,¹⁸ and $C_p^{\text{H}_2} = 112.85$ kc/sec for the spin-rotational constant of the proton in H_2 ,¹⁹ we obtain for $C_p^{\text{CH}_4}$ the value $+11.7$ kc/sec. This is very close to the experimental value of 10.40 kc/sec, the slight discrepancy being due to a change in the potential V_p between CH_4 and H_2 of 2.2 eV. If we took the negative value this would imply an unlikely shift in V_p of -35.5 eV. Thus we have $c_a = +10.40 \pm 0.10$ kc/sec and the additional fact that the proton in CH_4 lines in a potential 2.2 eV lower than in H_2 .

IV. PROTON IN CD_3H

A. Introduction

Since the spectrum of CH_4 gave only a measurement of c_a , it was necessary to investigate the proton in CD_3H to obtain independent information about the constants c_α and c_β . The analysis of the proton hyperfine structure in this molecule is simpler than in CH_4 , since there is only one proton and it lies on the axis of symmetry of a symmetric-top molecule. However, more rotational states are excited, and the spectrum observed is an envelope of a large number of lines which possesses a periodic structure. The semistatistical nature of this problem reduces the accuracy of the result even though the resonance curves are much quieter because of a small background problem.

B. The Hamiltonian, Eigenvalues, and Transition Frequencies

The Hamiltonian for the protons is

$$H = -\mathbf{u}_p \cdot \mathbf{H} - \hbar \mathbf{I}_p \cdot \mathbf{C}_p' \cdot \mathbf{J} - \frac{2\mu_p \mu_D}{I_p I_D R^3} \times \sum_{s,r} (-1)^r I_r^{s,p} R_{-r}^{s,p}. \quad (33)$$

¹⁸ J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance* (McGraw-Hill Publishing Company, New York, 1959).

¹⁹ N. J. Harrick, R. G. Barnes, P. J. Bray, and N. F. Ramsey, Phys. Rev. **90**, 260 (1953), and N. F. Ramsey, *ibid.* **90**, 232 (1953). The value 112.85 kc/sec is the difference between 113.904 kc/sec of the first paper and 1.059 kc/sec of the second.

Since the first term is much larger than the next two terms, a first-order high-field perturbation calculation can be used, giving for the first term the eigenvalues $-\mu_n g_p H m_I$.

The second term is the spin-rotational interaction, where

$$\mathbf{C}_{p'} = \begin{pmatrix} c_{\alpha'} & 0 & 0 \\ 0 & c_{\alpha'} & 0 \\ 0 & 0 & c_{\beta'} \end{pmatrix} \quad (34)$$

The eigenvalues for this term can be calculated using the vector model or simply taken from Townes and Schawlow²⁰ to give

$$-hm_I m_J \left[c_{\alpha'} + (c_{\beta'} - c_{\alpha'}) \frac{K^2}{J(J+1)} \right], \quad (35)$$

where K is the symmetric-top quantum number for the projection of J on the axis of symmetry.

The third term gives the dipole-dipole interaction between the proton and the three deuterons, and in general should be treated using the techniques developed in the last section. But using the distance of 1.79 Å and the magnetic moments of the proton and deuteron, it is found this term can spread the lines by at most about

9 kc/sec, and it usually spreads them less. Since the resolution of the apparatus was only 5 kc/sec this interaction is never resolved, so it will be treated as a broadening mechanism, though it might produce a slight shifting as well. Thus, ignoring this last term, the transition frequencies of the proton are given by

$$\nu = \nu_p + m_J \left[c_{\alpha'} + c_{d'} \frac{K^2}{J(J+1)} \right], \quad (36)$$

where

$$c_{d'} = c_{\beta'} - c_{\alpha'}.$$

C. A Semi-Statistical Model

A qualitative idea of the shape of the spectrum may be obtained from the following simple model. The number of molecules in the state J, K in the range $dKdJ$ for a given value of m_J is given by

$$dN = AdJdK \exp \left\{ -\frac{B_x J(J+1) + (B_z - B_x) K^2}{kT} \right\}. \quad (37)$$

Making the change in variable from K to $(\nu - \nu_p) = \nu'$ and integrating over all allowed J we have for each value of m_J the line shape

$$I(\nu', m_J) = I_0 \exp \left\{ -\frac{B_x m_J^2}{kT} \left[1 + \left(\frac{B_z}{B_x} - 1 \right) \left(\frac{\nu' - m_J c_{\alpha'}}{|m_J| c_{d'}} \right) \right] \right\} / \left\{ [c_{d'} m_J (\nu' - m_J c_{\alpha'})]^{1/2} \left[1 + \left(\frac{B_z}{B_x} - 1 \right) \left(\frac{\nu' - m_J c_{\alpha'}}{m_J c_{d'}} \right) \right] \right\} \quad (38)$$

with the restriction that

$$0 \leq \frac{(\nu' - m_J c_{\alpha'})}{c_{d'} m_J} < 1$$

which comes from

$$0 \leq \frac{K^2}{J(J+1)} < 1.$$

For $m_J = 0$, this analysis is not valid and what we have is just a single broadened line at the Larmor frequency.

For $c_{\alpha'} m_J > 0$, $I(\nu', m_J)$ has a singular point at $\nu' = m_J c_{\alpha'}$ and trials off, either to the right or left of this point, depending on whether $c_{\alpha'}$ and $c_{d'}$ have the same or opposite signs, approximately as

$$\frac{I_0 \exp(-B_x m_J^2 / kT)}{|\nu' - m_J c_{\alpha'}|^{1/2}}. \quad (39)$$

The total resonance curve then is a single line at the Larmor frequency plus a sum of the $I(\nu') m_J$ terms for $m_J = \pm 1, \pm 2, \dots$.

It will have broadened peaks at the points $\nu' = m_J c_{\alpha'}$

and the region between the central peak and the points $\pm c_{\alpha'}$ will be either relatively clear or filled in depending on whether $c_{\alpha'}$ and $c_{d'}$ have the same or opposite signs.

D. The Experiment

The experimental conditions for the proton resonance in CD_3H were similar to those for the CH_4 run at 78°K, except that the beam was detected by the CD_3H^+ ion at mass 19. The gas, supplied by Merck Ltd. of Canada, had a stated purity of 98% CD_3H , and since no other isotopic form of methane has an ion fragment at mass 19 the resonance curves were attributed only to CD_3H . The optimum rf current was found to be about 1 A; however the shape of the resonance was found to be relatively independent of rf power, in contrast to the CH_4 resonance.

One of the best curves is shown in Fig. 5. The most notable feature is the appearance of regularly spaced peaks approximately every 10 kc/sec giving $c_{\alpha'} = \pm 10$ kc/sec. Also, the central peak is not standing alone, so it appears that $c_{\alpha'}$ and $c_{d'}$ have opposite signs.

E. Discussion of the CD_3H Results

To relate the spin-rotational tensors in two molecules containing different isotopes, we note that these tensors

²⁰ C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Publishing Company, New York, 1955).

are related to the strength of the magnetic field generated at a nucleus per unit of angular momentum, whereas the fields are generated by the angular velocity of the charges. Thus the product of the spin-rotational tensor times the moment-of-inertia tensor (taken in that order) is an invariant tensor under isotope changes, as can also be seen by the expression in Townes and Schalow.²⁰ This is true only if corrections for vibrations and stretching are ignored. Therefore, the constants c_{α}' and c_{β}' for the CD_3H molecule are given in terms of the spin-rotational constants for the CH_4 molecule, as defined in the first section, by

$$\begin{aligned} c_{\alpha}' &= c_{\alpha}/1.6, \\ c_{\beta}' &= c_{\beta}/2.0. \end{aligned}$$

Using these relationships, the measured value for $c_{\alpha} = \frac{1}{3}(2c_{\alpha}' + c_{\beta}') = +10.40$ kc/sec, and the observation that $c_{\alpha}' \pm 10$ kc/sec, we find that either

$$(a) \quad c_{\alpha}' = -10.4 \text{ kc/sec} \quad \text{for} \quad c_{\alpha}' = +10.0 \text{ kc/sec}$$

or

$$(b) \quad c_{\alpha}' = +41.6 \text{ kc/sec} \quad \text{for} \quad c_{\alpha}' = -10.0 \text{ kc/sec.}$$

Both are consistent with the experimental observation that c_{α}' and c_{α} have opposite signs. Statistical-model calculations were made for these two cases and gave curves which favored the first possibility but were not conclusive.

A calculation for the nuclear framework of positive charges gives a value of $+3.7$ kc/sec for c_{β} . Any shielding by the electrons would tend to reduce this quantity, and so it should be a reasonable upper limit. Notice that the first possibility above implies $c_{\beta}' = -0.4$ kc/sec, a very reasonable value, whereas the second gives $c_{\beta}' = +31.6$ kc/sec, which is highly unlikely.

A detailed calculation of all the lines in the region between 15 and 35 kc/sec for

$$\nu' = m_J [(10.0 - 10.4K^2)/J(J+1)]$$

gave two groups of lines, the first centered at 18 kc/sec and the second at 27 kc/sec. The average of ten experimental curves gave peaks at 19.4 ± 0.1 kc/sec and 29.8 ± 0.2 kc/sec. Thus a value for c_{α}' of $\frac{1}{2}[(19.42/18) + (29.77/27)]10 = 10.9$ kc/sec is a better value for this constant. Using this value for c_{α}' with an uncertainty of ± 1.0 kc/sec, we now find that the components of the CH_4 spin-rotational tensor are

$$c_{\alpha} = 17.4 \pm 1.6 \text{ kc/sec,}$$

and

$$c_{\beta} = -3.6 \mp 3.2 \text{ kc/sec.}$$

It should be pointed out that although the statistical-model comparison gives some weight to the physical argument outlined above, we really have no clear experimental evidence which explicitly rules out the second possibility for the sign of c_{α}' , which gives for the components of the CH_4 spin-rotational tensor the values

$$c_{\alpha} = -17.4 \pm 1.6 \text{ kc/sec,}$$

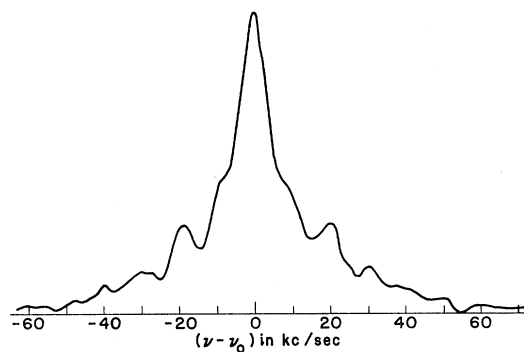


FIG. 5. Proton magnetic resonance spectrum in CHD_3 at 78°K .

and

$$c_{\beta} = +66.0 \mp 3.2 \text{ kc/sec.}$$

V. THE DEUTERON'S QUADRUPOLE INTERACTION IN METHANE

A. CD_4

The deuteron resonance in CD_4 was run in the hope of measuring the quadrupole coupling constant of a deuteron in methane.

Since the deuteron has a much smaller magnetic moment than the proton, higher rf currents are needed to induce transitions. The 3-in. coil used in the proton measurements, however, would overheat with the higher currents to such a degree that it would outgas enough to scatter the beam. Thus the shorter $\frac{3}{4}$ -in. coil which was water-cooled had to be used, resulting in an intrinsic resolution of about 20 kc/sec for a CD_4 beam at 78°K and 30 kc/sec for the beam at room temperature.

Unfortunately, what was observed at both temperatures was a single resonance line only slightly broader than the intrinsic widths. And the slight amount of broadening could be accounted for by the spin-rotational interaction, this interaction being smaller in CD_4 because of a larger moment of inertia than in CH_4 and the smaller magnetic moment of the deuteron.

This single narrow line can be explained by considering the quadrupole interaction, which can be written in spherical tensor form as

$$H_Q = \frac{eQ}{2I(2I-1)} \sum_{s=1}^4 \sum_r (-1)^r I_r^s q_{-r}^s, \quad (40)$$

where the I_r^s are components of the tensor of rank 2 formed from the spin vector of nucleus s , and q_r^s are the components of the electric field gradient at nucleus s . To put this interaction into an irreducible form of the molecular point group we need only note that the above tensors depend only on the single nuclear coordinate s and hence are isomorphic to the vectors \mathbf{r}_s directed to the nuclei, which we have shown can be put into the

forms A_1+F_2 . The scalar or A_1 -symmetry quadrupole interaction must vanish for reasons identical to the ones given for the scalar dipole-dipole interaction, and so the quadrupole interaction has only F_2 symmetry. The diagonal matrix elements of this term vanish for the spin states of symmetry type A_1 and E , and are in general nonvanishing for the F_1 - and F_2 -symmetry spin states. (The spin states CD_4 can be shown to have the reduction $15A_1+6E+3F_1+15F_2$.) Thus it is possible that the type- F states are spread out so much that they are not observed, while the type- A_1 and $-E$ states, which show no quadrupole interaction, are broadened only slightly by the spin-rotational interaction.

This difference can be enhanced even more by the fact that the sensitivity for a $\Delta m = \pm 1$ transition was slightly less than optimum for the apparatus, because of the small magnetic moment of the deuteron. Thus multiple transitions would be detected with greater sensitivity, and these would occur mainly for the A_1 and E spin states and all resonances near the Larmor frequency. This type of distortion has been seen before.^{13a} Because of these difficulties, no definite conclusion about the quadrupole coupling constants for a deuteron in methane could be obtained with CD_4 .

It might be assumed that the same behavior would also occur in all spherical-top molecules, in particular a molecule like CCl^{35}_4 . But in CD_4 the centrifugal distortion term is larger than the quadrupole coupling constant for all J , whereas in CCl^{35}_4 the centrifugal distortion energies are probably smaller than the quadrupole coupling terms, which are typically tens of megacycles. Thus in CCl^{35}_4 the symmetry numbers are no longer good quantum numbers because the quadrupole Hamiltonian will mix states of symmetry A and E with the F states.

B. The Deuteron in CH_3D

Because of the failure of CD_4 to yield any definite information about the quadrupole coupling constant, the deuteron in CH_3D was investigated. This molecule should have been ideal because of the relatively simple analysis for a single particle on an axis of symmetry, but experimental difficulties made its deuteron resonance very noisy. First there was a large background problem at the masses 17 (CH_3D^+) and 16 (CH_2D^+) due to OH^+ and O^+ , and there was a relatively small

signal at mass 15 (CH_3^+ and CHD^+). Another difficulty was the fact that the deuteron has a small magnetic moment compared to the three protons and so the large deflection fields, necessary to deflect the deuteron, have their imperfections or aberrations magnified by the protons. In spite of these difficulties a noisy resonance was observed which spanned about 150 kc/sec.

The maximum deviations from the Larmor frequency ν_D is given by $\pm \frac{3}{4} eqQ$. Using the value for the maximum extent of the resonance curve of ± 75 kc/sec gives $eqQ \cong 100$ kc/sec. This seems quite small for the quadrupole interaction of the deuteron compared with its value in other molecules.

VI. THE CH_4 ROTATIONAL MAGNETIC MOMENT

When considering the general Hamiltonian for CH_4 in Sec. II there was the term $-\mathbf{u}_J \cdot \mathbf{H}$ which gives the interaction of the rotational magnetic moment μ_J with the external field. An rf field at the Larmor frequency $\mu_n g_J H/h$ will induce Δm_J transitions which could be detected by the apparatus if $\Delta m_J g_J$ was about 1 nm. The detection of small rotational magnetic moments by using multiple-quantum transitions has been reported previously.²¹

A search with the $\frac{3}{4}$ -in. rf coil gave a resonance which corresponds to a g of about 0.31 nm and so transitions of $\Delta m_J \gtrsim 3$ must have occurred. The line was not strong and only slightly broader than the intrinsic linewidth of the rf coil. A number of runs calibrated against the deuteron in D_2 gave $|g_J| = 0.3133 \pm 0.0002$.

There have been microwave Zeeman measurements of the component of the g tensor along the axis of symmetry of the molecules $H-C \equiv C-CH_3$ and $D-C \equiv C-CH_3$ giving the values $|g_{zz}| = 0.298 \pm 0.006$ and $|g_{zz}| = 0.31 \pm 0.01$, respectively,²² which are consistent with the above measurement for CH_4 . Weltner²³ pointed out this correspondence sometime ago and using a comparison with the susceptibility measurements obtained the reasonable result that the sign of the g value is probably positive.

²¹ R. A. Brooks, C. H. Anderson, and N. F. Ramsey, *Phys. Rev. Letters* **10**, 441 (1963).

²² J. T. Cox, P. B. Peyton, Jr., and W. Gordy, *Phys. Rev.* **91**, A22 (1953); J. T. Cox and W. Gordy, *ibid.* **101**, 1298 (1955).

²³ W. Weltner, Jr., *J. Chem. Phys.* **24**, 918 (1956); **28**, 477 (1958).