≪Orginal≫ The Spin-Rotation Interaction of the Proton and the Fluorine Nucleus in the Tetrahedral Spherical Top Molecules

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Abstract

The spin-rotation constants of the proton and the fluorine nucleus in CH_4, SiH_4, GeH_4, CF_4, SiF_4 and GeF_4 were determined experimentally by the molecular beam magnetic resonance method. From the Hamiltonian and the high field approximation, the quantized energy level is given by the following equation.

$$W_{m_I m_J} = -g_I m_I H - g_J m_J H - c_{av} m_I m_J,$$

where c_{av} is one third of the trace of the C tensor. In the nuclear resonance experiment, the proton and the fluorine nuclear resonance curves consist of many unresolved lines given by $\nu = -g_J H - c_{av} m_I$, and a Gaussian approximation is made to correlate c_{av} to the experimentally obtained half-width of the resonance curve. In the rotational resonance experiment, the five resonance peaks as predicted by $\nu = -g_I H - c_{av} m_I$, $m_I = 0$, ± 1 and ± 2, were all observed. The magnitude of c_{av} was determined by measuring the frequency distance between two adjacent peaks. The sign of c_{av} was determined by the side peak suppression technique. The technique is described, and the sign and magnitude of the spin-rotation constant c_{av} are summarized as following;

for CH_4 -10.3 ± 0.4 kHz (from the rotational resonance),
for SiH_4 $+3.71 \pm 0.08$ kHz (from the nuclear resonance),
for GeH_4 $+3.79 \pm 0.13$ kHz (from the nuclear resonance),
for CF_4 -6.81 ± 0.08 kHz (from the rotational resonance),
for SiF_4 -2.46 ± 0.06 kHz (from the rotational resonance),
and finally for GeF_4 -1.84 ± 0.04 kHz (from the rotational resonance).

요   약

AX₄型分子인 CH₄, SiH₄, GeH₄, CF₄, SiF₄ 및 GeF₄의 陽子 또는 弗素原子核의 spin 과 分子의 廻轉사이의 相互作用의 크기를 나타내는 spin-rotation constant c_{av} 를 分子線磁氣共鳴方法에 依하여 實驗的으로 決定하였다. 强磁場近似에 依한 Hamil-

tonian 은

$$W_{m_I m_J} = -g_I H - g_J m_J H - Ca v m_I m_J$$

로 주어지며, c_{av} 는 C tensor 의 trace 의 3분지 1이 된다. 原子核磁氣共鳴曲線은 $\nu = -g_I H - c_{av} m_J$ 로 주어지는 여러개의 廻轉共鳴線의 重疊으로 이룩되며, 全體曲線 은 Gauss 曲線으로 近似하여 c_{av} 값을 求하였다.

廻轉共鳴線은 $\nu = g_J H - c_{av} m_I$ 로 주어지며, m_I 는 0, ±1, ±2의 값을 갖는다. c_{av} 의 크기는 隣接하는 두 廻轉共鳴曲線사이의 振動數差로서도 求할수 있다. 本實驗에서 原子核共鳴과 廻轉共鳴 共히 利用되였다. c_{av} 의 符號는 分子線磁氣共鳴實驗에서 쓰이 는 方法으로서, 量子化되여서 不均一磁場에서 分離된 分子線을 進行하는 方向의 左側 또는 右側에서 部分的으로 遮斷하면서, 共鳴曲線의 變化를 보는것으로, 決定된 符號 와 c_{av} 의 크기는 다음과 같다.

CH₄; −10.3±0.4kHz　SiH₄; +3.71±0.08kHz

GeH₄; +3.79±0.13kHz　CF₄; −6.81±0.08kHz

SiF₄; −2.46±0.06kHz　GeF₄; −1.84±0.04kHz

1. Introduction

Anderson[1] investigated the spin-rotation interaction in CH_4 and found the magnitude of the spin-rotation constant c_{av}, to be 10.40 ±0.1kHz. This value was obtained from the resolved structure of the nuclear resonance curve. The present work is the extension of their work to the molecules, CH_4, SiH_4, GeH_4, CF_4, SiF_4 and GeF_4 which all have the tetrahedral spherical symmetry. The nuclei at the centers of mass of the molecules have zero spin as the small fractions of isotopes which have non zero spin are neglected. The Hamiltonian in the unit of frequency was discussed in the separate paper on the rotational magnetic resonance experiment[2] and is given by

$$H = -g_I \vec{I}\vec{H} - g_J \vec{J}\vec{H} - C_{av}\vec{I}\vec{J} \qquad (1)$$

and, at high field approximation[3]

$$W_{m_I m_J} = -g_I m_I H - g_J m_J H - C_{av} m_I m_J, \qquad (2)$$

where $\vec{I} = \sum_{i=1}^{4} \vec{I}_i$ for 4 spins of the protons or fluorine nuclei at the periphery of the molecule, and c_{av} is 1/3 of the trace of the C tensor which has the following experssion

$$C = \begin{pmatrix} c_{xx} & 0 & 0 \\ 0 & c_{yy} & 0 \\ 0 & 0 & c_{zz} \end{pmatrix}, \qquad (3)$$

and here $c_{xx} = c_{yy} \ncong c_{zz}$ as the nuclear spin is not at the center of mass of the molecule but located at the periphery of the spherical top molecule. The analytical expressions of the diagonal elements of the C tensor were discussed in detail by Townse and Schawlow[4], and Schwarz[5].

The energy levels of the spin-rotation interaction and the spin-spin interaction in the AX_4 type spherical top molecule were derived group theoretically by Yi, Ozier, and Anderson[6], and on the basis of those energy levels, the spin-rotation constants were worked out by Ozier, Crapo, and Lee[7] from the nuclear reson ancedata. The present paper is to determine those constants and their signs experimentally by using both the nuclear magnetic resonance method and the rotational magnetic resonance method.

2. The Gaussian Approximation to the Nuclear Resonance Curve

Unless c_{av} is larger than the intrinsic broadening of the resonance line, as is the present case, the resonance curve is the result of superposition of many unresolved lines given by $\nu = -g_I H - c_{av} m_J$ for the nuclear transition of $\Delta m_I = \pm 1$. In this nuclear resonance frequency equation derived from the high field approximation, m_J may extend to a large

Table 1.   **Constants used in the nuclear magnetic resonance experiment**

Molecule	Source temp. (°K)	Moment of inertia, A	$B=\dfrac{h^2}{8\pi^2 AkT}$	$v_p=\sqrt{\dfrac{2kT}{M}}$	$J_p=\dfrac{1}{2}\left(\sqrt{\dfrac{2}{B}}-1\right)$	r_o [8]
CH$_4$	292	0.5227×10^{-39}	0.002639	55.1×10^3	3.86	1.09
SiH$_4$	//	0.9692	0.001423	38.9	5.45	1.48
GeH$_4$	//	1.036	0.001331	25.2	5.65	1.53
CF$_4$	//	14.65	0.00009413	23.5	22.6	1.32
SeF$_4$	//	20.21	0.00006824	21.6	26.6	1.55
GeF$_4$	//	23.45	0.00005881	18.1	28.7	1.67

v_p: The most probable molecular velocity

J_p: The most probable J value

r_o: The distance from the central atom to that at the periphery.

value as the result of the large moment of inertia of the polyatomic molecule. In the case of CH$_4$, however, Anderson[1] resolved m_J dependent structure at the liquid nitrogen temperature, but in the cases of all other molecules treated in the present experiment, they were not resolved, and an expression is required to correlate the experimentally obtained half-width to the magnitude of the spin-rotation constant.

The mechanical rotational energy of the molecule is $2J+1$ fold degenerated with respect to the Zeeman effect, consequently the number of molecules in J state is given by the weighted Boltman's law as follows.

$$(2J+1)e^{-BJ(J+1)}, \quad B=\frac{h^2}{8\pi^2 AkT} \qquad (5)$$

In this expression the samall nuclear and rotational magnetic interaction energies are ignored and h and A are the Planck's constant and the moment of inertia of the molecules, respectively. Then the number of molecules in m_J state can be obtained by summing up over J not smaller than the given m_J. Namely,

$$N_{m_J}=\sum_{J=m_J}(2J+1)e^{-BJ(J+1)}$$

$$=\sum_{J=0}-\sum_{J=0}^{m_J-1}=N_0-N_1, \qquad (6)$$

$$N_1\cong\frac{1}{B}(1-e^{Bm_J(m_J-1)}), \quad N_0=1/B.$$

so that

$$N_{m_J}=e^{-Bm_J(m_J-1)}\approx e^{-Bm_J^2}.$$

N_{m_J} multiplied by the Rabi transition probability[3] between two Zeeman levels gives the resonance curve.

The resonance curve is thus approximated with the Gaussian curve, which leads to the following relation between the experimental half-width, δ. and c_a,

$$|c_{av}|=\frac{\delta}{2\sqrt{\dfrac{\log2}{B}}} \qquad (7)$$

The numerical values of B in the equation (7) were calculated from the molecular constants and given source temperatures shown in the Table 1 and the half-width were obtained from the nuclear resonance curves. c_{av} thus obtained are summarized in the Table 2.

The sign of the spin-rotation constant may

Table 2. The spin-rotation constants determined by nuclear resonance experiments

Molecular	$|c_{av}|$ (kHz)
CH$_4$	—
SiH$_4$	3.71 ± 0.08
GeH$_4$	3.79 ± 0.13
CF$_4$	6.36 ± 0.30
SiF$_4$	2.46 ± 0.10
GeF$_4$	1.84 ± 0.07

be discussed in connection with the magnetic shielding and the chemical shift data[9-11] in NMR. From this consideration, the signs of CH_4 and CF_4 may be decided to be positive for the former and negative for the latter. However, the positive sign thus given to c_{vv} of CH_4 is found to be inconsistent, but the negative sign given to c_{av} of CF_4 is consistent with the result of the present investigation. The experimental determination of the sign of the spin-rotation constant is presented in the next section.

3. The Rotational Resonance Experiment for c_{av} and the Determination of the Sign of the Spin-Rotation Constant

The resonance frequency of the rotational magnetic resonance is given by

$$\nu = -g_J H - c_{av} m_I, \qquad (8)$$

were $m_I = 0, \pm 1$ and ± 2. All five resonance peaks corresponding to those quantum numbers of m_I were observed, so that c_{av} can be obtained from the frequency distance between two adjacent peaks. However, as the second side peaks($m_I = \pm 2$) are weak, the centering is found difficult, so that c_{av} was obtained using $m_I = 0$ peak and $m_I = \pm 1$ peaks. c_{av} thus obtained are tabulated in the Table 3 with the number of independent data and the standard deviation, and the experimental counditions are summarized in the Table 4.

Since in the inhomogeneous magnetic field in the molecular beam magnetic resonance

Table 3. The spin-rotation constant determined by the rotational magnetic resonance

Molecule	Number of independent values	c_{av}(kHz)	Resolution of the peaks
CH_4	17	10.3±0.4	complete
SiH_4	26	3.8±0.4	incomplete
GeH_4	16	4.0±0.2	nearly complete
CF_4	24	6.81±0.08	complete
SiF_4	32	2.46±0.06	nearly complete
GeF_4	22	1.84±0.04	nearly complete

apparatus, the beams of positive m_I and those of negative m_I take the opposite paths, it is possible to eliminate the beams of positive $m_I = +1$ and $+2$ by using a suitable obstackle. As the result, the resonance peaks at one side must disappear in the resonance curve, traced out in the recorder. If c_{av} is positive, this disappearence of the peaks or the suppression of the side peaks has to take place at the lower frequency side, as g_J is negative[2] for all six molecules investigated in this experiment.

The elimination of the beams with $m_I \neq 0$ was achieved successfully obtaining very distinct suppression of the side peaks at either side of the contral resonance peak. The experimental technique is simply to screw in the side plate of the detector buffer slit toward the axis of the travellig beam. The whole range of the frequencys pectrum is then swept

Table 4. The experimental conditions in the rotational magnetic resonance experiment

Molecule	r_o(Å)[3]	Source temp. (°K)	Molecular mass	A	B	$v_p = \sqrt{\dfrac{2kT}{M}}$	J_p
CH_4	1.09	77	16.0	0.523×10^{-39}	0.0100	28.3×10^3	1.8
SiH_4	1.48	125	32.1	0.969	0.00332	25.5	3.4
GeH_4	1.53	134	76.6	1.04	0.00290	17.1	3.7
CF_4	1.32	125	88.0	14.7	0.000220	15.4	15
SiF_4	1.55	188	104.1	20.2	0.000106	17.3	21
GeF_4	1.67	165	148.6	23.5	0.000104	13.6	22

Table 5. The sign assignment to c_{av}

Molecule	Suppression	Sign assignment
CH_4	at higher frequency side	—
SiH_4	at lower frequency side	+
GeH_4	at lower frequency side	+
CF_4	at higher frequency side	—
SiF_4	at higher frequency side	—
GeF_4	at higher frequency side	—

Table 6. The final c_{av}

Molecule	c_{av}(kHz)
CH_4	-10.3 ± 0.4
SiH_4	$+3.71 \pm 0.08$
GeH_4	$+3.79 \pm 0.13$
CF_4	-6.81 ± 0.08
SiF_4	-2.46 ± 0.06
GeF_4	-1.84 ± 0.04

and the curve thus obtained is compared with the normal one. The result of the side peak suppression experiment is shown in the Table 5 together with the sign assignmen t of the spin-rotation constant.

4. Conclusion

Since the spin-rotation constants are obtained independently from the nuclear resonance experiment and the rotational resonance experiment, the final choice on c_{av} has to be made.

In the cases of SiF_4 and GeF_4 and GeF_4, the magnitudes obtained by the two different methods agree completely. Since those from the rotational resonance experiments gives smaller standard deviations, the values 2.46 ± 0.06 kHz for SiF_4 and 1.84 ± 0.04kKz for GeF_4 are taken as the final values of c_{av}. As the rotational resonance curve of CF_4 obtained in the present experiment is clean and the side peaks are completely resolved, the value from the rotational resonance should be more accurate than that from the nuclear resonance and take 6.81 ± 0.08kHz for the final value. The nuclear resonance experiment for CH_4 is not carriedout in the present experiment, because it was performed previously with suf ficient accaurcy. However, the c_{av} is obtained from the rotational resonance experiment and found to be 10.3 ± 0.4kHz which is the final value. The rotational resonance curve of SiH_4

were least resolved and the standard deviation is large, so that the value from the nuclear resonance experiment is taken as the final value which is 3.71 ± 0.08kHz. with the similar reason, we take 3.79 ± 0.13kHz for c_{av} of GeH_4 as the final. These final values of c_{av} together with the signs are tabulated in Table 6.

It is shown that the sign assignment of c_{av} is done experimentally with good success. The side peak suppression technique is the direct method of determining the sign. The sign assignment often carried out by referrng to the chemical shift data in NMR could be erroneous.

Unless the spin-rotation constant is smaller than the line-width, the rotational resonance experiment could give the magnitude of c_{av} in a more convenient way, since in this experiment, c_{av} is determined without any involvement of the constants of the molecule and the temperature of the beam.

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