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Microwave Zeeman Effect of Formaldehyde

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Zeeman effects in the absorption spectra of formaldehyde H_2CO , HDCO, and D_2CO were studied in microwave region with magnetic field of 1500~300 oersteds. The effective g -values in several rotational states and the elements of g -tensor g_{aa} , g_{bb} , and g_{oo} of these molecules were determined.

Dependences of the effective g -values on the rotational quantum numbers J, τ were consistent among these isotopically substituted molecules. The components of the g -tensors of these molecules have been found to be $g_{aa}=2.86\pm 0.04$ for H_2CO , 2.00 ± 0.05 for HDCO, and 1.46 ± 0.05 for D_2CO . They are extraordinarily large compared to those of other molecules already known. A brief qualitative interpretation is given.

§ 1. Introduction

The electronic ground states of formaldehyde H_2CO , HDCO, and D_2CO are $^1\Sigma$. These

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molecules have rotational magnetic moments of the order of nuclear magnetons due to the end-over end rotation. The magnetic hyperfine structures observed by the molecular beam maser experiment¹⁾ are small, so that it is reasonable to neglect the hyperfine structures in considering the Zeeman effect,

Theories of Zeeman effects of such \sum -molecules have been given by several authors^{2,5}). The Zeeman energy of a molecule in an external magnetic field H is

$$W = -\mu_n g_J M H, \quad (1)$$

where μ_n is the nuclear magneton, M the magnetic quantum number of the rotational angular momentum J , and g_J the effective g -factor in a given rotational state. The g -factor g_J is expressed as⁵

$$g_J = \frac{1}{2} \left\{ 1 + \frac{1}{J(J+1)} \left[E(\kappa) - (\kappa+1) \frac{dE(\kappa)}{d\kappa} \right] \right\} g_{aa} + \frac{1}{J(J+1)} \frac{dE(\kappa)}{d\kappa} g_{bb} + \frac{1}{2} \left\{ 1 - \frac{1}{J(J+1)} \left[E(\kappa) - (\kappa-1) \frac{dE(\kappa)}{d\kappa} \right] \right\} g_{cc}, \quad (2)$$

where κ is Ray's asymmetry parameter and $E(\kappa)$ is defined by the formula of the energy of an asymmetric rotor

$$W = \frac{1}{2} (A+C)J(J+1) + \frac{1}{2} (A-C)E(\kappa). \quad (3)$$

The element of the g -tensor $g_{\mu\nu}(\mu, \nu = a, b, c)$ is given by a formula⁴),

$$g_{\mu\nu} = \frac{M_p}{I_\nu} \left[\sum_K Z_{K\ell} (|X_{K\alpha}|^2 \delta_{\mu\nu} - X_{K\mu} X_{K\nu}) - \frac{1}{m} \sum_n \frac{\langle 0 | L_\mu | n \rangle \langle n | L_\nu | 0 \rangle + \langle 0 | L_\nu | n \rangle \langle n | L_\mu | 0 \rangle}{E_n - E_0} \right], \quad (4)$$

where I_ν is the moment of inertia around a -axis and M_p is the mass of proton. The first term of the right hand side of Eq. (4) is the nuclear contribution to the magnetic moment and the summation is to be taken over all nuclei, where $X(X_{K\alpha}, X_{K\beta}, X_{K\gamma})$ is the position of K -th nucleus with electronic charge $Z_{K\ell}$. The second term is the electronic contribution due to the partial excitation of electronic state by the rotation of molecule and the summation is to be taken over every possible electronic excited state where L_μ , or L_ν , is the electronic angular momentum around μ - or ν -axis. The observed lines are those of electric dipole transitions between K -type doubling levels and the microwave electric field is perpendicular to the dc magnetic field in the present experimental apparatus.

The selection rules in this case are

$$\Delta J = 0, \quad \Delta M = \pm 1, \quad \Delta K_{-1} = 0, \quad (5)$$

and the transition frequencies are

$$\nu = \nu_0 - \frac{\mu_n M}{h} (g_1 - g_2) M \mp \frac{\mu_n}{h} g_1 H, \quad (6)$$

where ν_0 is the frequency for the pure rotational transition and g_1 and g_2 are the g -values of upper and lower levels, respectively.

The g -factor of an asymmetric molecule can be expressed by a g -tensor with nonvanish-

ing off-diagonal elements $g_{\mu\nu}(\mu \neq \nu)$. However, such a molecule with C_{2v} symmetry as H_2CO and D_2CO has a diagonal g -tensor.

§ 2. Experiment and Analysis

A 5000 Mc wave guide (2.5 cm \times 5 cm) absorption cell of 100 kc Stark modulation type was inserted in a solenoidal coil of 35 cm length and of 7 cm inner diameter. The magnetic field strength was 165 ± 3 oersteds/ampere, and the current of 10~20 A was applied. The magnetic field was measured by an electronic fluxmeter. The sinusoidal Stark-modulation with dc bias electric field was used to observe the lines. To obtain the Zeeman pattern of the spectral lines the observed frequencies were extrapolated to those for zero electric field⁶). Each line was observed to split into two components in a magnetic field, and no further splittings of each component nor broadening of the lines, as is expected from the second terms on the right hand side of Eq. (4), were observed. Thus the difference of the g -values for the upper and lower levels could not be found, that is, $g_1 - g_2 \approx 0$. The central frequency of the two components are calculated as $\nu_0 \pm ((g_1 + g_2)/2h)\mu_n H$ considering the frequencies and relative intensities of all transitions between various M -states. Effective g -values

Table I. *g*-factors in various transitions of formaldehyde.

Molecules	Transitions	Frequencies (Mc)	Effective <i>g</i> -values in terms of g_{aa} , g_{bb} , g_{cc} of H ₂ CO (calc)	Effective <i>g</i> -factors (obs)	Effective <i>g</i> -factors (calc)
H ₂ CO	1 _{1,1} → 1 _{1,0}	4829.73	0.5000 g_{aa} +0.2500 g_{bb} +0.2500 g_{cc}	1.50±0.02	1.53
	2 _{1,2} → 2 _{1,1}	14488.65	0.1667 g_{aa} +0.4167 g_{bb} +0.4167 g_{cc}	0.615±0.02	0.622
HDCO	1 _{1,1} → 1 _{1,0}	5346.64	0.3495 g_{aa} +0.2473 g_{bb} +0.2208 g_{cc}	1.13±0.01	1.10
	2 _{1,2} → 2 _{1,1}	16038.06	0.1164 g_{aa} +0.3835 g_{bb} +0.3680 g_{cc}	0.49±0.01	0.47
	5 _{2,4} → 5 _{2,3}	4489.08	0.0934 g_{aa} +0.4186 g_{bb} +0.3621 g_{cc}	0.38±0.01	0.41
D ₂ CO	1 _{1,1} → 1 _{1,0}	6096.10	0.2516 g_{aa} +0.2100 g_{bb} +0.1950 g_{cc}	0.83±0.02	0.80
	2 _{1,2} → 2 _{1,1}	18287.90	0.0839 g_{aa} +0.3500 g_{bb} +0.3250 g_{cc}	0.36±0.02	0.36
	4 _{1,3} → 4 _{2,2}	3682.28	0.1003 g_{aa} +0.3100 g_{bb} +0.2914 g_{cc}	0.39±0.01	0.39

in terms of the elements of *g*-tensor were obtained by the Eq. (2) using the rotational constants of these molecules obtained in this laboratory⁷). The effective *g*-values of isotopically substituted molecules are expressed in terms of a *g*-tensor of any one molecule, because it is plausible to assume same electronic structures for the isotopically substituted molecules. In Table I *g*-values expressed in terms of g_{aa} , g_{bb} , and g_{cc} of H₂CO are listed.

Table II. *g*-values of formaldehydes.

Molecules	g_{aa}	g_{bb}	g_{cc}
H ₂ CO	2.90±0.05	0.35±0.10	0.02±0.10
HDCO	2.00±0.05	0.32±0.10	0.02±0.10
D ₂ CO	1.46±0.05	0.29±0.10	0.02±0.10

The present experiment gives only absolute values of the effective *g*-tensors, which are shown in the next to the last column in Table I. If it is assumed, however, that all the observed effective *g*-factors have the same signs, the elements of *g*-tensor, g_{aa} etc, can be determined by the following procedure.

First solving six equations in Table I by the method of least mean square with the above assumptions, the absolute values of

$g_{\mu\nu}$'s are calculated as in Table II, where the g_{aa} and g_{bb} are found to have the same signs, and the magnitude of g_{cc} is quite small. It can be shown from Eq. (4) that $g_{\mu\nu}$ can not be larger than +1, and if $|g_{\mu\nu}| > 1$, $g_{\mu\nu}$ must be negative. This may be the case if the magnitude of the electronic term in Eq. (4) is sufficiently large. Therefore the signs of g_{aa} and g_{bb} are concluded to be negative.

The effective *g*-factors calculated from the equations in Table I and the values of g_{aa} , g_{bb} , and g_{cc} in Table II are in close agreement with the experimental results as shown in the last column of Table I.

§ 3. Discussions

With the aid of Eq. (4), the diagonal elements of *g*-tensor can be expressed as

$$\frac{I_a}{2M_p} g_{aa} = \sum_{\kappa} \frac{Z_{\kappa}}{2} (b_{\kappa}^2 + c_{\kappa}^2) - \frac{1}{m} \sum_n' \frac{|\langle 0 | L_a | n \rangle|^2}{E_n - E_0} \quad (7)$$

with similar expressions for g_{bb} and g_{cc} . The left hand side of Eq. (7) and the first term on the right hand side can be calculated from the molecular constants and *g*-values in Table II. The calculated electronic contributions are shown in Table III. If the inner shell

Table III. The nuclear and electronic contributions to the magnetic moment of H₂CO.

	nuclei	electrons	total
	$\sum_{\kappa} \frac{Z_{\kappa}}{2} (X_{\kappa} ^2 \bar{g}_{\mu\nu} - X_{\kappa} \mu^2)$	$-\frac{1}{m} \sum_n' \frac{ \langle 0 L_{\mu} n \rangle ^2}{E_n - E_0}$	$\frac{I_{\mu}}{2M_p} g_{\mu\mu}$
<i>a</i> -axis	0.92 Å ²	-3.47 Å ²	-2.56 Å ²
<i>b</i> -axis	3.9	-0.1	-2.2
<i>c</i> axis	4.8	-5.1	+0.3

electrons are assumed to be fixed to the nuclei and valence electrons to the middle of the bonds, the second term in Eq. (7) is transformed into

$$-\frac{1}{2} \sum_i (x_{ib}^2 + x_{ic}^2)$$

where x_{ib} and x_{ic} are coordinates of the i -th electron.

Although such a "frozen" charge approximation does not give correct values of

Table IV. Molecular g Factors for Hydride Molecules in 1Σ States.

Molecule	g (observed)	g (calculated by a frozen charge approximation)
H ₂	+0.8829±0.00007 ^a	+1.00
NH ₃	$g_{zz}=0.484±0.0007^b,c$	+0.50
	$g_{xx}=g_{yy}=0.560±0.007^c$	+0.60
H ₂ O	$g_a=0.585^b,d$	+0.60
	$g_{bb}=0.742^b,d$	+0.50
	$g_{cc}=0.666$	+0.51
H ₂ S	$g_{aa}=±0.355±0.008^e$	+0.56
	$g_{bb}=±0.195±0.008^e$	+0.50
	$g_{cc}=±0.209±0.008^e$	+0.53
CH ₃ CCH	$g_{zz}=0.298^f$	+0.50
	$g_{xx}≈0$	+0.09
CH ₃ F	$g_{zz}=0.487$ or 0.612^g	+0.50
	$g_{xx}=±0.0624^g$	+0.07
H ₂ CO	$g_{aa}=-2.90±0.05$	+0.50
	$g_{bb}=-0.35±0.10$	+0.08
	$g_{cc}=0.02±0.10$	+0.13

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g -factors, it is interesting to see that this assumption can explain qualitatively the observed g -factors of almost all hydride molecules. This assumption, however, fails in the estimation of g -value in the case of formaldehyde, as is shown in the Table IV⁸⁾. It will be due to the neglect of the contribution of two electrons bonding carbon and oxygen atoms, and a lone pair of electrons around the oxygen atom, whose positions are considered to be protruding out of the molecular axis. They give negative magnetic moments when the molecule rotates around a -axis. If the valence electrons bonding carbon and hydrogen atoms are assumed to be fixed at the middle of the bonds, the effective mean radius of these four electrons, a couple of π -electrons and a lone pair of electrons, is

$$r_{\text{eff}} = \frac{1}{2} \sqrt{\frac{I_a}{M_p} |g_{aa}| + (b^2 + c^2)} = 1.2 \text{ \AA},$$

which seems to be a reasonable value.

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