

## MILLIMETRE WAVE SPECTRUM OF METHYL MERCURY CHLORIDE\*

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The  $J = 16 \rightarrow 17$  rotational transition has been studied for  $\text{CH}_3\text{HgCl}^{35}$  for the most abundant mercury isotopes. These measurements lead to new values for the spectral constants  $B_0$  and  $D_{jk}$  and to values for  $D_{jj}$  the distortion constant associated with end-over-end rotation.

Previous studies<sup>1, 2, 3</sup> on mercuric compounds have indicated that the  $\sigma$ -bonding orbitals of the mercury atom are  $sp$ -hybridized. It was shown by Gordy and Sheridan<sup>4</sup> from the pure rotation spectra of methyl mercury chloride and bromide that these molecules are symmetrical tops. This indicated unequivocally that in them the C—Hg—Halogen grouping is strictly linear. In their study the  $B_0$ 's were calculated from the general symmetric top formula

$$\nu_0 = 2B(J + 1) - 4D_{jj}(J + 1)^3 - 2D_{jk}(J + 1)K^2,$$

neglecting the centrifugal distortion term  $4D_{jj}(J + 1)^3$ . This term has now been measured for the methyl mercury chloride molecules containing Hg (198, 199, 200 and 202), and new values obtained for the rotational constants.

$\text{Hg}^{201}$  is the only Hg isotope with a nuclear quadrupole moment. Because of its small natural abundance (13.2 %) and the splitting of the lines by nuclear quadrupole coupling the intensity of the lines is expected to be small and the assignment of the  $\text{CH}_3\text{Hg}^{201}\text{Cl}$  spectrum difficult. An attempt has been made to unravel the spectrum and an indication of the probable value of the  $\text{Hg}^{201}$  nuclear quadrupole coupling constant obtained.

### EXPERIMENTAL

The sample of methyl mercury chloride was the one used in the previous microwave study by Gordy and Sheridan.<sup>4</sup> The microwave spectra were observed with a frequency sweep spectrometer employing a video type detector.<sup>5</sup> Crystal harmonic generators<sup>6</sup> driven by reflex Klystron tubes were used as energy sources. Frequencies were measured with a standard monitored by comparison with the standard 5-Mc/s signal of the National Bureau of Standards station WWV.

Methyl mercury chloride is a solid with a vapour pressure of  $1.6 \times 10^{-2}$  mm at  $27^\circ \text{C}$ .<sup>7</sup> The substance was allowed to evaporate into the evacuated wave-guide cell at room temperature.

### SPECTRAL CONSTANTS

The  $J = 16 \rightarrow 17$  transition of  $\text{CH}_3\text{HgCl}^{35}$  was studied. This particular transition was chosen because the splitting by the chlorine coupling is negligible and only one major Cl line is obtained for each  $K$  value when  $\Delta F = +1$ . A large number of frequencies were observed owing to the large number of abundant mercury isotopes and the nuclear

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quadrupole hyperfine structure due to  $\text{Hg}^{201}$ . Several observed lines not accounted for in the course of this work probably arise from molecules in an excited (bending) vibrational state.

In tables 1 and 2 are listed the lines observed<sup>4</sup> for the  $J = 8 \rightarrow 9$  and for the  $J = 16 \rightarrow 17$  rotational transitions of methyl mercury chloride, together with the calculated values obtained using the spectral constants determined from these transitions and given in table 3.

TABLE 1.—FREQUENCIES OF THE LINES OF THE  $J = 8 \rightarrow 9$  ROTATIONAL TRANSITION OF  $\text{CH}_3\text{HgCl}^{35}$  FOR  $K = 0$

mercury isotope	$\nu_0$ (obs.) Mc/s	$\nu_0$ (calc.) Mc/s
198	37394.00	37393.99
199	37388.40	37388.40
200	37382.80	37382.80
202	37371.60	37371.60

#### CENTRIFUGAL DISTORTION CONSTANTS

Interaction of the rotations of the molecule about the  $A$  and  $B$  axes (fig. 1) is responsible for the energy term containing  $D_{jk}$ . Since  $D_{jk} > 0$  the effective moment of inertia  $I_b$  of the molecule about the  $B$ -axis increases with  $K$ . This effect is opposite to that expected

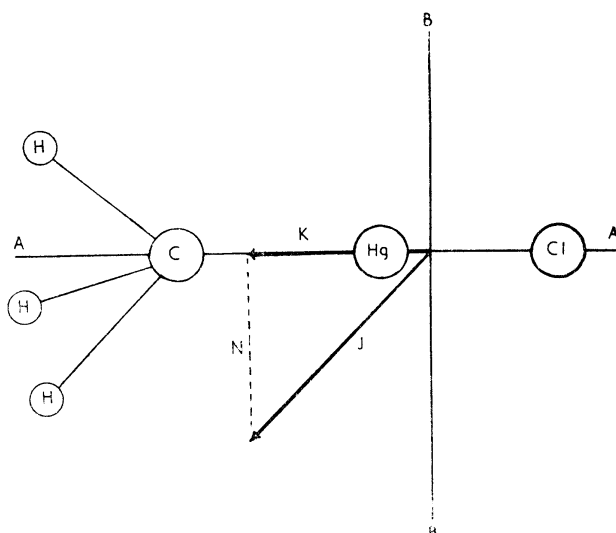


FIG. 1.—The methyl mercury chloride molecule.

on simple grounds, since an increase in  $K$  would be expected to decrease  $\alpha$  and thus decrease  $I_b$ . For the methyl halides it has been shown by Thomas, Cox and Gordy<sup>8</sup> that the positive sign of  $D_{jk}$  is explicable in terms of a shifting of the internal energy of the molecule from one bond to another.

The mechanism of distortion of the molecule as it rotates is described thus. As  $K$  increases so does the angular momentum about the  $A$ -axis. The increased centrifugal force acting on the hydrogens of the methyl group tends to make the  $\text{CH}_3$  group more nearly planar. Effectively the  $s$ -character of the three carbon orbitals which bond to hydrogen is increased. To offset this the  $s$  character of the carbon orbital bonding to the mercury must be reduced for proper normalization. The combined effect of the hybridization changes at the carbon atom is to increase the bond stretching force constant of the  $\text{C—H}$  bonds and to decrease that of the  $\text{C—Hg}$  bond. The effect of changes in size and shape of the  $\text{CH}_3$  group upon  $I_b$  can be neglected in comparison with the effect of changes in the  $\text{C—Hg}$  bond length. An increase of only  $0.0012 \text{ \AA}$  in the  $\text{C—Hg}$  bond length would suffice to account for the  $17.89 \text{ kc/s}$  separation of the  $K = 0$  and  $K = 5$  lines in the  $J = 16 \rightarrow 17$  transition of  $\text{CH}_3\text{Hg}^{200}\text{Cl}^{35}$ . If this increase is due entirely to a change in the covalent radius of the carbon atom it corresponds to a decrease of about  $0.7\%$  in  $s$  character (or increase in  $p$  character) of the carbon orbital. This small hybridization change would be sufficient to account for the needed  $\text{C—Hg}$  bond lengthening.

TABLE 2.—FREQUENCIES OF THE LINES OF THE  $J = 16 \rightarrow 17$  ROTATIONAL TRANSITION OF  $\text{CH}_3\text{HgCl}^{135}$

isotope	Hg <sup>199</sup>		Hg <sup>200</sup>		Hg <sup>202</sup>	
	$\nu$ (obs.) Mc/s	$\nu$ (cal.) Mc/s	$\nu$ (obs.) Mc/s	$\nu$ (cal.) Mc/s	$\nu$ (obs.) Mc/s	$\nu$ (cal.) Mc/s
$K$						
0	70629.71	70629.70	70618.92	70618.92	70608.29	70587.33
1	70629.03	70628.99	70618.32	70618.21	70607.58	70586.61
2	70626.86	70626.84	70616.02	70616.06	70605.45	70584.46
3	70623.21	70623.27	70612.46	70612.49	70601.86	70580.88
4	70618.31	70618.28	70607.56	70607.50	70596.92	70575.86
5					70590.40	70590.37

TABLE 3.—OBSERVED SPECTRAL CONSTANTS OF  $\text{CH}_3\text{HgCl}$

constant	Hg <sup>199</sup>		Hg <sup>200</sup>		Hg <sup>202</sup>	
	$B_0$ (Mc/s)	$D_{jj}$ (kc/s)	$B_0$ (Mc/s)	$D_{jj}$ (kc/s)	$B_0$ (Mc/s)	$D_{jj}$ (kc/s)
$B_0$ (Mc/s)	2077.48 $\pm$ 0.01		2077.18 $\pm$ 0.01		2076.86 $\pm$ 0.01	2076.24 $\pm$ 0.01
$D_{jj}$ (kc/s)	0.241 $\pm$ 0.01		0.256 $\pm$ 0.01		0.259 $\pm$ 0.01	0.245 $\pm$ 0.01
$D_{jk}$ (kc/s)	21.0 $\pm$ 0.10		21.0 $\pm$ 0.10		21.1 $\pm$ 0.10	21.1 $\pm$ 0.10

From this change in hybridization an increase of about  $22'$  in  $\angle$  HCH and a decrease of  $0.0004 \text{ \AA}$  in the C—H bond length respectively would be expected. The latter would be partly compensated by the centrifugal force tending to lengthen the C—H bonds. Since the molecule is a symmetric top, in the ground vibrational state, the CHgCl grouping is linear and no hybridization changes occur at the Hg atom. This implies that the HgCl bond length does not vary with  $K$  and hence the effects described are confined to the CH<sub>3</sub>—Hg grouping.

Similar arguments applied to the end-over-end rotation lead one to conclude that the C—Hg would be shortened and  $D_{jj}$  negative. Since  $D_{jj}$  is positive in value it seems clear that the much more rapid rotation of the molecule about the  $A$  axis is more effective in distorting the HCH angles and thus varying the state of hybridization of the carbon atom than is the end-over-end rotation. The effect of the end-over-end rotation would be to decrease the magnitude of  $D_{jj}$ . It should be pointed out that the effect of the HCH-angle distortion on the C—Hg bond-length will also tend to be cancelled by the lengthening of the C—Hg—Cl grouping due to centrifugal distortion.

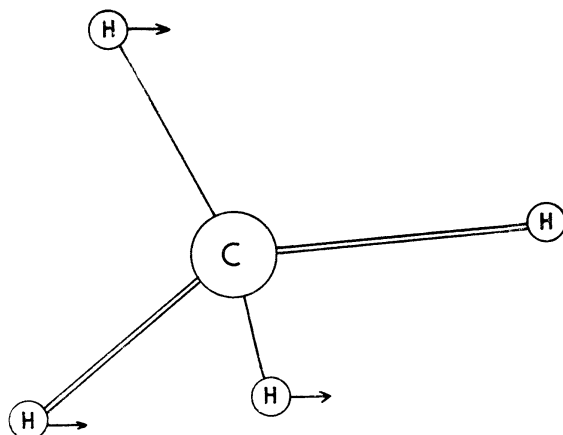


FIG. 2.—Bending vibration of CH<sub>4</sub> molecule during which orbital following by change of carbon hybridization is possible.

bending vibrations. Linnett and Wheatley concluded that bending vibrations will occur more easily if the bonding orbitals are able to follow the movement of the atoms by a change of hybridization. They showed that in methane it is possible for the bonding orbitals to follow the atoms during certain vibrations by change of hybridization. In particular, it was found that for the bending vibration illustrated in fig. 2 the carbon bonding orbitals were able, by change of hybridization, to follow the attached hydrogen atoms.

When we examine the motion of the methyl mercury chloride molecule as  $K$  increases it is seen that the hydrogen atoms move in precisely the same direction with respect to each other as they do in the vibrational bending mode illustrated in fig. 2.

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