Microwave Spectrum of Propargyl Halides. I. Molecular Structure, Dipole Moment, and Quadrupole Coupling Constant of Propargyl Chloride

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The C—Cl bond length in propargyl chloride $CH_2ClC\equiv CH$ was found by Pauling, Gordy and Saylor¹⁾ to be 1.82±0.02 Å. It is remarkably longer than C—Cl lengths observed in a number of other aliphatic chlorides. However, the value obtained in the previous paper²⁾, 1.7802 Å, was close to the usual C—Cl bond length.

The present paper will include the observation and the analysis of rotational spectra of two other isotopic species, $CH_2{}^{35}ClC\equiv CD$ and $CH_2{}^{37}ClC\equiv CD$, and will give a molecular structure more reliable than the previous one.

Experimental

The spectrometer used was similar to that reported by Shimoda, Nishikawa and Itoh³⁾. A 100 Kc. sine wave modulation was used. The microwave was generated by klystrons, 2K26, 2K25, 8V77, X-12, and X-13, and the frequency was multiplied by a silicon crystal. The frequency range covered was from 7000 Mc./sec. to 36000 Mc./sec. An X-band absorption cell of 3 m. in length was employed, and the Stark electrode was supported by Teflon tape grooved at its center. The spacing between the electrode and the cell was not measured, but the calibration was made by observing the Stark effect of the $J=1\rightarrow 2$ lines of carbonyl sulfide $^{16}O^{12}C^{32}S$ at 24325.94 Mc./sec.⁴⁾. The vacuum system was designed in such a way that the sample flew continuously through the cell, its pressure being estimated by a Pyrani gauge. The cell was cooled with dry ice when necessary. The frequency of microwave was measured by the technique developed by Shimoda⁵⁾. The out-put power of microwave was detected by another silicon crystal and fed into a narrow band amplifier tuned with 100 Kc./sec. and then detected by a phase-sensitive detector. The signal was amplified by a low-frequency amplifier and observed on a cathode ray oscilloscope or on a recorder. The ultimate sensitivity was about $5\times 10^{-9}\,cm^{-1}$ when the recorder was used⁶⁾.

Propargyl chloride was synthesized by Dr. T. Shimozawa by the chlorination of propargyl alcohol⁷⁾. The deuterated species $CH_2ClC\equiv CD$ was obtained by mixing normal propargyl chloride with heavy water which was made slightly alkaline by adding a small quantity of anhydrous sodium carbonate.

Results

Rotational Spectra and Rotational Constants. —Propargyl chloride is a nearly prolate symmetric top, and the a- and b- axes are in the

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3) K. Shimoda, T. Nishikawa and T. Itoh, *J. Phys. Soc. Japan*, **9**, 974 (1954).

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TABLE I. OBSERVED AND CALCULATED FREQUENCIES OF THE SPECTRA IN THE GROUND VIBRATIONAL STATE (Mc./sec.)*

	$CH_2{}^{35}ClC\equiv CH$		$CH_2{}^{37}ClC\equiv CH$		$CH_2{}^{35}ClC\equiv CD$		$CH_2{}^{37}ClC\equiv CD$	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
a-Type								
$2_{0,2}\rightarrow 3_{0,3}$	17559.47	17559.49	17194.93	17195.16	16494.03	16494.16	16153.62	16153.69
$2_{1,2}\rightarrow 3_{1,3}$	17117.51	17117.56	16769.44	16767.89	16085.85	16085.84	15758.59	15758.66
$2_{1,1}\rightarrow 3_{1,2}$	18023.22	18023.67	17643.00	17644.90	16919.85	16922.17	16567.43	16567.27
$3_{0,3}\rightarrow 4_{0,4}$	23397.48	23397.50					21526.20	21525.66
$3_{1,3}\rightarrow 4_{1,4}$	22819.59	22819.50			21444.19	21444.31	21008.84	21008.26
$3_{1,2}\rightarrow 4_{1,3}$	24028.26	24027.56	23520.91	23520.66				
$3_{2,2}\rightarrow 4_{2,3}$	23429.2_0	23428.80						
$3_{2,1}\rightarrow 4_{2,2}$	23460.52	23460.76						
$4_{0,4}\rightarrow 5_{0,5}$	29222.29	29222.55	28617.83	28618.03	27452.20	27452.01	26887.05	26886.87
$4_{1,4}\rightarrow 5_{1,5}$	28518.24	28518.16	27936.00	27936.02	26800.23	26779.84	26255.39	26255.11
$4_{2,3}\rightarrow 5_{2,4}$	29281.78	29281.64	28672.8	28673.52	27504.77	27504.40	26936.60	26936.20
$4_{2,2}\rightarrow 5_{2,3}$	29345.7_0	29345.55			27560.52	27560.76	26988.42	26989.13
$4_{3,1}\rightarrow 5_{3,2}$ $4_{3,2}\rightarrow 5_{3,3}$	29302.15	29302.58	28694.4	28693.31	27523.16	27523.20	26953.83	26954.03
$4_{1,3}\rightarrow 5_{1,4}$			29394.00	29394.71	28193.52	28193.40		
b-Type								
$2_{0,2}\rightarrow 2_{1,1}$					21067.5	21067.11		
$3_{0,3}\rightarrow 3_{1,2}$					21495.43	21495.16	21364.7	21365.02
$4_{0,4}\rightarrow 4_{1,3}$	22921.58	22921.47						
$5_{0,5}\rightarrow 5_{1,4}$	23727.87	23726.87			22816.32	22817.10		
$6_{0,6}\rightarrow 6_{1,5}$	24719.31	24719.17	24508.91	24508.92	23728.20	23729.56	23520.15	23521.57
$7_{0,7}\rightarrow 7_{1,6}$	25911.16	25911.93	25656.94	25657.54	24822.98	24825.12	24575.30	24577.65
$8_{0,8}\rightarrow 8_{1,7}$	27319.22	27320.31	27011.07	27012.77	26114.84	26117.23	25819.24	25822.33
$9_{0,9}\rightarrow 9_{1,8}$	28958.40	28960.73	28587.43	28590.16	27615.44	27620.62	27263.97	27269.54
$0_{0,0}\rightarrow 1_{1,1}$	27077.01	27077.01	26868.46	26868.46	26008.25	26008.25	25797.49	25797.49
$7_{1,7}\rightarrow 8_{0,8}$	29132.01	29130.87						
$11_{2,10}\rightarrow 12_{1,11}$	17442.95	17435.36						
$12_{2,11}\rightarrow 13_{1,12}$	25079.7	25072.4						

* The centrifugal distortion is assumed to be $-D_{JK}J(J+1)K_{-1}^2-D_JJ^2(J+1)^2$, with $D_{JK}=-0.057$ Mc./sec. and $D_J=0.0021$ Mc./sec.

TABLE II. ROTATIONAL CONSTANTS AND PRINCIPAL MOMENT OF INERTIA IN THE GROUND VIBRATIONAL STATE*

	$CH_2{}^{35}ClC\equiv CH$	(Calcd.)**	$CH_2{}^{37}ClC\equiv CH$	(Calcd.)**	$CH_2{}^{35}ClC\equiv CD$	(Calcd.)**	$CH_2{}^{37}ClC\equiv CD$	(Calcd.)**
A	24299.28	(24300.75)	24146.48	(24144.91)	23396.70	(23396.74)	23238.18	(23236.39)
B	3079.77	(3080.72)	3013.80	(3014.82)	2890.33	(2890.24)	2828.85	(2828.84)
C	2777.73	(2778.31)	2721.98	(2722.64)	2611.55	(2611.56)	2559.31	(2550.40)
b_P	-7.06709×10^{-3}		-6.85720×10^{-3}		-6.75178×10^{-3}		-6.56026×10^{-3}	
I_a	20.80436		20.93601		21.60694		21.75433	
I_b	164.146		167.739		174.904		178.705	
I_c	181.994		185.722		193.575		197.526	

* Rotational constants are given in Mc./sec. and principal moments of inertia in amu Å^2. Conversion factor 505531 Mc./sec. amu Å^2 is used.

** Values are calculated by using the set of structure parameters (I) given in Table V.

symmetry plane. Thus the dipole moment has components along the a- and b-axes, and transitions of both a- and b-types are observed. The observed spectra are listed in Table I, where center frequencies are given. The assignment is made mainly by the b-type Q-branch series, $J_{0,J}\rightarrow J_{1,J-1}$. The quadrupole hyperfine structure due to chlorine atom is of some use to check the assignment.

The b-type Q-branch series mentioned above give the rotational constants $[A-(B+C)/2]$ and the asymmetry parameters b_P, whereas the constants $B+C$ and $B-C$ are obtained by measuring the a-type R-branch lines. The

$0_{0,0} \rightarrow 1_{1,1}$ lines are important since their frequencies are equal to $A+C$. The rotational constants and the asymmetry parameters are given in Table II, where the moments of inertia are calculated by using the conversion factor 505531 Mc./sec. amu Å^2. The frequencies calculated by using these rotational constants are compared with the observed ones in Table I.

In the course of searching, the spectra of two excited vibrational states were found. By comparing their intensities with those of the ground state, one is assigned to the CCCl bending mode and the other to one of the C—C≡C bending modes. The center frequencies and the rotational constants derived from them are listed in Table III.

TABLE III. OBSERVED AND CALCULATED FREQUENCIES OF THE SPECTRA AND ROTATIONAL CONSTANTS IN THE EXCITED VIBRATIONAL STATES ($CH_2{}^{35}ClC \equiv CH$) (Mc./sec.)

	State I (δCCCl)		State II (δCC≡C)	
	Obs.	Calcd.	Obs.	Calcd.
$2_{0,2} \rightarrow 3_{0,3}$	17597.0	17592.7	17545.4	17545.4
$0_{0,0} \rightarrow 1_{1,1}$	27230.76	27230.8		
$6_{0,6} \rightarrow 6_{1,5}$	24926.32	24926.7		
$7_{0,7} \rightarrow 7_{1,6}$	26141.31	26142.4		
$8_{0,8} \rightarrow 8_{1,7}$	27576.77	27578.2	27184.66	27185.2
$9_{0,9} \rightarrow 9_{1,8}$			28809.18	28810.5
$A(\alpha_i)$	24450.2	(−150.9)	24214.6	(84.7)
$B(\beta_i)$	3088.1	(−8.3)	3076.09	(3.68)
$C(\gamma_i)$	2780.6	(−2.9)	3776.60	(1.13)
b_P	-7.14570×10^{-3}		-7.03413×10^{-3}	

Structure Analysis. — The structure of propargyl chloride is specified by eight parameters: C—Cl, C—C, C≡C, methylenic C—H, and acetylenic C—H bond lengths, and CCCl, HCH and CCH bond angles, the C—C≡C—H group being assumed to be linear. The distance between two hydrogen atoms in methylene group is directly given by the quantity $[(I_a+I_b-I_c)/m_H]^{1/2}$. The four kinds of isotopic species give fairly close values for the distance, as shown in Table IV. However, as Laurie pointed out$^{8)}$, the inertia defect Δ makes this distance short and the angle HCH apparently small. Since the data on the isotopic molecules for which deuterium is substituted in the methylene group were not available, it was difficult to see how much the inertia defect was. If the value is assumed to be 0.2194 amu Å as found for chloroacetonitrile$^{9)}$, the distance H···H becomes 1.7715 Å. In the following the molecular structure is calculated by assuming Δ equal to zero or 0.2194 amu Å^2.

TABLE IV. THE HYDROGEN TO HYDROGEN DISTANCE IN METHYLENE GROUP

	$I_a+I_b+I_c$ (amu Å^2)	H···H (Å)
$CH_2{}^{35}ClC \equiv CH$	2.956	1.712_3
$CH_2{}^{37}ClC \equiv CH$	2.953	1.711_4
$CH_2{}^{35}ClC \equiv CD$	2.936	1.706_5
$CH_2{}^{37}ClC \equiv CD$	2.933	1.705_6

The inertia defect arises from the zero-point vibration, and it is accepted from the case of water molecule$^{10)}$ that the contribution of low-frequency vibrations to inertia defect is larger than those of high-frequency ones. The CCCl and C—C≡C bending modes are mentioned as the low-frequency vibrations in propargyl chloride, and the rotational constants are obtained in the excited states of these two vibrations as stated above. It is interesting to see how much the inertia defect and the distance H···H are changed if the rotational constants are corrected for these two vibrations. The corrected rotational constants, A', B', and C', are given by

$$A' = A_0 + (1/2)(\alpha_1 + \alpha_2)$$

$$B' = B_0 + (1/2)(\beta_1 + \beta_2)$$

and

$$C' = C_0 + (1/2)(\gamma_1 + \gamma_2)$$

where α_1, β_1, γ_1 and α_2, β_2, γ_2 denote the changes of rotational constants due to the two vibrations. Their observed values are 24266.2 Mc./sec., 3077.5 Mc./sec. and 2776.8 Mc./sec., respectively. The H···H distance, 1.738 Å, calculated by using A', B' and C' is in fact fairly larger than that obtained by A_0, B_0 and C_0, 1.709 Å, but still smaller than 1.772 Å which was obtained by assuming $\Delta = 0.2194$ amu Å^2.

The parameters other than the H···H distance, seven in number, are to be determined by the remaining eight constants. Not all parameters can be determined by the present data, hence several assumptions are necessary. It is recognized that the C≡C bond length is relatively constant, irrespective of the attached groups. The value 1.207 Å is assumed for this length$^{11,12)}$. The acetylenic C—H bond length makes a small contribution to the rotational constants, hence the value 1.06 Å is assumed for this distance without strong influence upon other parameters to be obtained$^{12)}$. The lengths, C—H and C—D, are assumed to be the same. The groups C—C≡C and C—C≡N are usually considered linear, though the detailed investigations gave slightly bent structures$^{13)}$. Here the

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10) B. T. Darling and D. M. Dennison, *Phys. Rev.*, **57**, 128 (1940). See also Ref. 8.

11) G. Herzberg and B. P. Stoicheff, *Nature*, **175**, 79 (1955).

12) C. C. Costain and B. P. Stoicheff, *J. Chem. Phys.*, **30**, 777 (1959).

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linear structure is also assumed. Two additional assumptions are the methylenic C—H bond length equal to 1.09 Å and the CCH bond angle equal to 111°30′. These two parameters, especially the latter, affect considerably the rotational constant A, in spite of the light weight of a hydrogen atom. Hence some precaution must be taken for selecting the assumed values for these parameters.

First, the inertia defect is set equal to zero. The methylenic C—H bond length and the CCH bond angle are assumed to be 1.09 Å and 111°30′, respectively. The eight rotational constants, A and C for each isotopic molecule, are used to determine the C—Cl and the C—C bond lengths, and the CCCl bond angle. They are found to be 1.7800 Å, 1.4582 Å, and 112°9′, respectively (Table V). If the bond lengths C—Cl and C—C become longer, both A and C decrease, on the other hand the A increases and the C decreases with the increase of the CCCl angle. Thus the determination of the CCCl angle is definite, but it is somewhat difficult to determine two bond lengths separately. Still it is feasible to obtain fairly good results for the two bond lengths. The fitting of the calculated constants with the observed is carried out by the least-squares method, the mean deviation is 0.00051 Å for the C—Cl bond length, 0.00062 Å for the C—C bond length, and 0.54′ for the CCCl bond angle. If the assumed value for the C≡C length, 1.207 Å, is in error by 0.01 Å, the C—Cl is changed by 0.001 Å, the C—C by 0.007 Å, and the CCCl by 2.5′.

TABLE V. STRUCTURE PARAMETERS UNDER VARIOUS ASSUMPTIONS

Set	Assumption		Result		
	Δ amuÅ^2	∠CCH	C—Cl Å	C—C Å	∠CCCl
I	0	111°30′	1.7800	1.4582	112° 9′
II$_a$	0.2194	107°30′	1.7728	1.4766	111°43′
II$_b$	0.2194	109°30′	1.7768	1.4724	111°45′
II$_c$	0.2194	111°30′	1.7808	1.4690	111°44′

Other assumptions
C≡C 1.207 Å
C—H (methylenic) 1.09 Å
C—H=C—D (acetylenic) 1.06 Å
C—C≡C—H(D) linear

Thus far, the analysis gives reasonable results. However, the inertia defect is by no means equal to zero, and its effect is obvious if the HCH angle is calculated to be 103°14′ by using the observed H···H distance 1.709 Å and the assumed C—H (methylenic) distance 1.09 Å.

In the second place, the inertia defect is assumed to be 0.2194 amu Å^2. This value is borrowed from the result for the chloroacetonitrile molecule. An analysis by the least-squares method is carried out by using three values for the CCH angle, 107°30′, 109°30′ and 111°30′. The methylenic C—H length is fixed to 1.09 Å. As stated above, the HCH angle becomes 108°42′, a quite reasonable value. The results obtained for the C—Cl and the C—C lengths, and the CCCl angle are listed in Table V. The CCCl bond angle is relatively independent of the values assumed for the CCH angle; however, the two bond lengths are varied by 0.008 Å. It is difficult to say which case is the most reasonable, but the length of the C—C bond adjacent to the triple bond is reported about 1.460 Å in a number of related molecules[11,12]. In this respect the case 111°30′ for the CCH angle is the most favorable, where the C—C length is 1.4690 Å. It is yet by no means clear whether or not the assumed value for the inertia defect is reasonable. It is felt that the inertia defect slightly less than 0.2194 amu Å^2 is more reasonable, since the C—C bond length then becomes somewhat shorter than 1.4690 Å. The parameter values, which are considered the most reasonable at present, are given in the last column of Table VI, where errors are attached by taking into account the zero-point vibration, inadequacy of the assumed parameters, and so on.

TABLE VI. MOLECULAR STRUCTURE

C—Cl	1.780±0.003 Å
C—C	1.465±0.007 Å
CCCl	111°50′±20′
HCH	108°42′±1°
CCH	111°30′±1°30′

Assumptions
C≡C 1.207 Å
C—H (methylenic) 1.09 Å
C—H(D) (acetylenic) 1.06 Å
C—C≡C—H(D) linear

Quadrupole Coupling Constant of Chlorine Atom. — The chlorine nuclear quadrupole coupling constant is determined by measuring the hyperfine structure of eight rotational transitions of the most abundant species $CH_2{}^{35}ClC{\equiv}CH$. By the lack of accidental degeneracy in rotational energy only the two components of the coupling constant, χ_{aa} and χ_{bb}, are obtained. The least-squares method gives $\chi_{aa} = -30.4$ Mc./sec. and $\chi_{bb} = -7.5$ Mc./sec. The hyperfine structures calculated by using these values are compared with the observed ones in Table VII.

A similar analysis is carried out on the hyperfine structures of eight transitions of $CH_2{}^{35}ClC{\equiv}CD$, but it is found that the values -28.2 Mc./sec. and -9.7 Mc./sec., which are

TABLE VII. HYPERFINE STRUCTURES OF THE CHLORINE NUCLEAR QUADRUPOLE COUPLING CONSTANT (Mc./sec.)

Transition	$F'' \rightarrow F'$		$CH_2{}^{35}ClC\equiv CH$			$CH_2{}^{35}ClC\equiv CD$		
			Obs.	Calcd.*	Calcd. − Obs.	Obs.	Calcd.**	Calcd. − Obs.
$2_{12}\rightarrow 3_{13}$	7/2	9/2	+1.08	+1.09	+0.01	+1.08	+1.05	−0.03
	5/2	7/2	−0.88	−0.83	+0.05	−0.57	−0.74	−0.17
	3/2	5/2	−2.34	−2.28	+0.06	−2.56	−2.25	+0.31
	1/2	3/2	−0.28	−0.36	−0.08			
$3_{21}\rightarrow 4_{22}$	9/2	11/2	+0.97	+1.05	+0.08			
	7/2	9/2	−1.82	−1.85	−0.03			
	5/2	7/2	−0.74	−0.81	−0.07			
	3/2	5/2	+2.08	+2.09	+0.01			
$3_{13}\rightarrow 4_{14}$	9/2	11/2				+0.80	+0.98	+0.18
	7/2	9/2				−0.07	−0.13	−0.06
	5/2	7/2				−1.00	−1.17	−0.17
$3_{03}\rightarrow 3_{12}$	7/2	7/2				+5.63	+5.26	−0.34
	5/2	5/2				+1.58	+1.58	0.00
	9/2	9/2				−2.92	−2.63	+0.29
	3/2	3/2				−6.52	−6.31	+0.21
$4_{04}\rightarrow 4_{13}$	9/2	9/2	+4.51	+4.52	+0.01			
	7/2	7/2	+1.95	+2.03	+0.08			
	11/2	11/2	−2.40	−2.59	−0.19			
	5/2	5/2	−5.16	−5.08	+0.08			
$5_{05}\rightarrow 5_{14}$	11/2	11/2	+4.07	+4.23	+0.16	+4.29	+4.37	+0.08
	9/2	9/2	+2.38	+2.29	−0.09	+2.15	+2.37	+0.22
	13/2	13/2	−2.69	−2.65	+0.04	−2.55	−2.73	−0.18
	7/2	7/2	−4.45	−4.59	−0.14	−4.61	−4.73	−0.12
$6_{06}\rightarrow 6_{15}$	13/2	13/2	+4.21	+4.10	−0.11	+4.24	+4.25	+0.01
	11/2	11/2	+2.65	+2.49	−0.16	+2.67	+2.57	−0.10
	15/2	15/2	−2.94	−2.74	+0.20	−2.92	−2.83	+0.09
	9/2	9/2	−4.45	−4.35	+0.10	−4.51	−4.50	+0.01
$7_{07}\rightarrow 7_{16}$	15/2	15/2	+4.02	+4.06	+0.04	+4.10	+4.21	+0.11
	13/2	13/2	+2.67	+2.66	−0.01	+2.67	+2.75	+0.08
	17/2	17/2	−2.84	−2.84	0.00	−2.86	−2.95	−0.09
	11/2	11/2	−4.25	−4.25	0.00	−4.30	−4.40	−0.10
$8_{08}\rightarrow 8_{17}$	17/2	17/2	+4.10	+4.08	−0.02	+4.30	+4.23	−0.07
	15/2	15/2	+2.85	+2.82	−0.03	+2.98	+2.92	−0.06
	19/2	19/2	−3.02	−2.97	+0.05	−3.09	−3.08	+0.01
	13/2	13/2	−4.24	−4.23	+0.01	−4.51	−4.38	+0.12
$9_{09}\rightarrow 9_{18}$	19/2	19/2	+4.06	+4.14	+0.08	+4.30	+4.29	−0.01
	17/2	17/2	+2.98	+2.98	0.00	+3.13	+3.09	−0.04
	21/2	21/2	−3.06	−3.11	−0.05	−3.22	−3.22	0.00
	15/2	15/2	−4.21	−4.26	−0.05	−4.46	−4.42	+0.04

* $\chi_{aa}=-30.4$ Mc./sec. and $\chi_{bb}=-7.5$ Mc./sec. are used.

** $\chi_{aa}=-28.2$ Mc./sec. and $\chi_{bb}=-9.7$ Mc./sec. are used.

calculated from coupling constants of $CH_2{}^{35}ClC\equiv CH$ by transforming the principal axes, explain the hyperfine structures sufficiently well.

If the values of χ_{aa} and χ_{bb} were accurate, the rotation of the principal axes due to the deuterium substitution might give the asymmetry parameter, but the present data do not warrant such a procedure. On the other hand, the second-order effect observed for the bromine nuclear quadrupole hyperfine structure of rotational spectra of propargyl bromide $CH_2BrC\equiv CH$ indicated that the asymmetry parameter was small[14]. The values of χ_{aa} and χ_{bb} obtained above give $\chi_{bond}=-75.8$ Mc./sec., under the assumption of the cylindrical symmetry of charge distribution about the C—Cl bond. The result is consistent with the value in the solid state, 71.6246 Mc./sec.[15]

Dipole Moment. — The dipole moment has two components; one along the a-axis and the other along the b-axis. The Stark effect of the $0_{0,0}\rightarrow 1_{1,1}$ transition of $CH_2{}^{35}ClC\equiv CH$ is measured to obtain the two components of the

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[14] Y. Kikuchi, E. Hirota and Y. Morino, *J. Chem. Phys.*, 31, 1139 (1959); This Bulletin, **34**, 348 (1961).

[15] T. Shimozawa, T. Chiba, I. Miyagawa and Y. Morino, ibid., to be published.

dipole moment. The presence of the chlorine nuclear quadrupole moment makes the Stark effect complicated, but it is possible to analyze the Stark effect of the $0_{0,0}\rightarrow 1_{1,1}$ transition, since the J number associated is small[16].

The quadrupole energy of the state $1_{1,1}$ is small, hence the weak, the intermediate, and the strong field cases are successively met with the increase of the Stark electric field. The quadrupole energy is zero for the state $0_{0,0}$.

The calculation of the Stark effect and the quadrupole effect is carried out by taking the wave function, $|IJ\tau M_J M_I>$, as the basis. The matrix elements of the Hamiltonian for the Stark effect H_E are diagonal in M_J and M_I, but they connect different rotational states. The state $0_{0,0}$ couples with states $1_{0,1}$ and $1_{1,1}$, and the state $1_{1,1}$ with states $1_{1,0}$, $2_{1,2}$, $0_{0,0}$, $2_{2,0}$ and $2_{0,2}$ by the Hamiltonian H_E. The differences in rotational energies are greater than the Stark or quadrupole energies, so that the second-order perturbation is sufficient to calculate the Stark effect[17]. Thus, it is reduced to the form;

$$\sum_{J'\tau'} \frac{|(IJ\tau M_J M_I|H_E|IJ'\tau' M_J M_I)|^2}{E_{J\tau}-E_{J'\tau'}}$$
$$=(\alpha+\beta M_J{}^2)\varepsilon^2$$

where ε is the Stark field strength, and α and β are constants depending upon the rotational constants, the rotational quantum numbers, and the dipole moment.

The Hamiltonian for the quadrupole energy, H_Q, has matrix elements, diagonal as well as nondiagonal with respect to M_J and M_I. Matrix elements between different rotational states are ignored, since the first-order perturbation is sufficient enough to treat the quadrupole energy. The matrix elements appropriate at present are as follows:

$$\begin{aligned}
&(IJ\tau M_J M_I|H_Q|IJ\tau M_J{}' M_I{}')\\
&\quad =P[3M_I{}^2-I(I+1)]\,[3M_J{}^2-J(J+1)]\\
&\qquad\qquad (M_J{}'=M_J,\ M_I{}'=M_I)\\
&\quad =P[3/2+3M_I M_J+3(M_I\mp 1)(M_J\pm 1)]\\
&\qquad \times\{[I(I+1)-M_I(M_I\mp 1)]\\
&\qquad \times[J(J+1)-M_J(M_J\pm 1)]\}^{1/2}\\
&\qquad\qquad (M_J{}'=M_J\pm 1,\ M_I{}'=M_I\mp 1)\\
&\quad =P(3/2)\{[J(J+1)-M_J(M_J\pm 1)]\\
&\qquad \times[J(J+1)-(M_J\pm 1)(M_J\pm 2)]\\
&\qquad \times[I(I+1)-M_I(M_I\mp 1)]\\
&\qquad \times[I(I+1)-(M_I\mp 1)(M_I\mp 2]\}^{1/2}\\
&\qquad\qquad (M_J{}'=M_J\pm 2,\ M_I{}'M_I\mp 2)
\end{aligned}$$

where P is given by

$$\begin{aligned}
P=\{&\chi_{aa}[J(J+1)+E(\kappa)-(\kappa+1)(\partial E(\kappa)/\partial\kappa)]\\
&+2\chi_{bb}(\partial E(\kappa)/\partial\kappa)\\
&+\chi_{cc}[J(J+1)-E(\kappa)\\
&+(\kappa-1)(\partial E(\kappa)/\partial\kappa)]\}/\\
&[4J(J+1)(2J-1)(2J+3)I(2I-1)]
\end{aligned}$$

which is reduced for the state $1_{1,1}$ to

$$P(1_{1,1})=-(1/60)\chi_{bb}$$

Secular determinant for the state $1_{1,1}$ factors into three groups, corresponding to $M_F=M_J+M_I=5/2$, $3/2$ and $1/2$, respectively. Secular determinants are all doubly degenerate. The case $M_F=5/2$ is the simplest, since the wave function belonging to $M_F=5/2$ is $|M_J, M_I>=|1, 3/2>$ or $|-1, -3/2>$. The secular equation is

$$3P+(\alpha+\beta)\varepsilon^2-W=0$$

The two pairs of wave functions, $[|\pm 1, \pm 1/2>$, $|0, \pm 3/2>]$, belong to $M_F=3/2$ and give rise to a two-dimensional secular equation:

$$\begin{vmatrix} -3P+(\alpha+\beta)\varepsilon^2-W & 3\sqrt{6}\,P \\ 3\sqrt{6}\,P & -6P+\alpha\varepsilon^2-W \end{vmatrix}=0$$

The wave functions corresponding to $M_F=1/2$ are $|\pm 1, \mp 1/2>$, $|0, \pm 1/2>$ and $|\mp 1, \pm 3/2>$, and the secular equation is

$$\begin{vmatrix} 3P+(\alpha+\beta)\varepsilon^2-W & -3\sqrt{6}\,P & 6\sqrt{3}\,P \\ -3\sqrt{6}\,P & 6P+\alpha\varepsilon^2-W & 0 \\ 6\sqrt{3}\,P & 0 & -3P+(\alpha+\beta)\varepsilon^2-W \end{vmatrix}=0$$

If the field strength ε is equal to zero, the secular equations give the following energy states:

$$\begin{array}{lll}
W_1=3P & F=5/2, & M_F=5/2\\
W_{21}=3P & 5/2, & 3/2\\
W_{22}=-12P & 3/2, & 3/2\\
W_{31}=3P & 5/2, & 1/2\\
W_{32}=-12P & 3/2, & 1/2\\
W_{33}=15P & 1/2, & 1/2
\end{array}$$

Here the representation $|IFM_I M_F>$ rather than $|IJM_I M_J>$ is good. There are only two states $|F, M_F>=|3/2, 1/2>$ and $|3/2, 3/2>$ possible in the rotational state $0_{0,0}$. Since the selection rule is $\Delta M_F=0$, transition to the state W_1 is forbidden and two pair states W_{21} and W_{31}, and W_{22} and W_{32} are degenerate, there are three hyperfine lines. If the Stark field increases so that the Stark energies $\alpha\varepsilon^2$ or $\beta\varepsilon^2$ are larger than P, the strong field case is apropppriate. The secular determinantes described above give the following states:

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16) F. Coester, *Phys. Rev.*, 77, 454 (1950).

17) S. Golden and E. B. Wilson, Jr., *J. Chem. Phys.*, **16**, 669 (1948).

$$\begin{array}{lcc} W_1=(\alpha+\beta)\varepsilon^2+3P & M_J=1, & M_I=3/2 \\ W_{21}=(\alpha+\beta)\varepsilon^2-3P & 1, & 1/2 \\ W_{22}=\alpha\varepsilon^2-6P & 0, & 3/2 \\ W_{31}=(\alpha+\beta)\varepsilon^2+3P & 1, & 3/2 \\ W_{32}=\alpha\varepsilon^2+6P & 0, & 1/2 \\ W_{33}=(\alpha+\beta)\varepsilon^2-3P & 1, & 1/2 \end{array}$$

This case can be expressed by the representation $|IJM_IM_J\rangle$. The rotational state $0_{0,0}$ involves two states $|M_J, M_I\rangle=|0, 1/2\rangle$ and $|0, 3/2\rangle$. Two transitions to the states $W_{22}(M_J=0, M_I=3/2)$ and $W_{32}(M_J=0, M_I=1/2)$ are allowed by the selection rules, $\Delta M_J=0$ and $\Delta M_I=0$.

The solutions for the intermediate case are obtained by solving the secular determinants given above. Eigenfunctions are obtained to calculate the transition probabilities. The change of the hyperfine patterns with the electric field, the frequencies and the intensities, is given in Fig. 1.

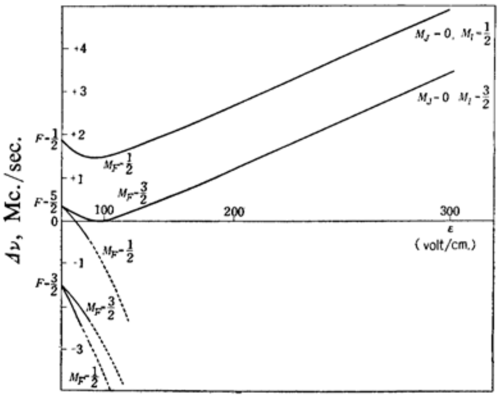

Fig. 1. Stark effect of the $0_{0,0}\rightarrow 1_{1,1}$ transition ($CH_2{}^{35}ClC\equiv CH$).

It is interesting to note that the transition to the state W_{21} in case $\varepsilon=0$ shifts first to lower frequency with increasing electric field, stops at some field strength ε_0, and then moves to a higher frequency. The observed intensity reduces to zero at ε_0, because the Stark modulation is used for the measurement. This is also the case for the transition to the state W_{33} at $\varepsilon=0$. The case $M_F=3/2$ is considered. The solutions are obtained by solving the secular equation, that is

$$W^{\pm}=-(1/2)\,[9P-(2\alpha+\beta)\varepsilon^2] \pm [(1/4)(3P+\beta\varepsilon^2)^2+54P^2]^{1/2}$$

The line mentioned above corresponds to the transition to the state W^+ and its frequency is given by

$$\nu=(W^+ +\alpha_0\varepsilon^2)/h$$

where $-\alpha_0\varepsilon^2$ is the Stark effect of the state $0_{0,0}$. Then the electric field ε_0, at which the Stark effect of the line changes its sign from minus to plus, is given by

$$\varepsilon_0{}^2=(P/\beta)\{-3-[216(2\alpha_0+2\alpha+\beta)^2/[\beta^2-(2\alpha_0+2\alpha+\beta)^2]]^{1/2}\}$$

The constants, α_0, α and β, are functions of two components of dipole moments, μ_a and μ_b. The Stark effect of the strong field case gives $\alpha_0+\alpha+\beta$ and ε_0 thus obtained provides another information on α_0, α and β.

The two components thus found are $\mu_a=0.98_5$ D and $\mu_b=1.36_0$ D, and the total moment $\mu_t=1.68$ D. There are four choices for the direction of the dipole moment, but it seems most plausible that the negative direction of the dipole moment lies between the C—Cl and the C—C≡C—H bonds, at an angle of 16±7° from the former. The total dipole moment 1.68 D is compared favorably with the value obtained by the dielectric constant measurement, 1.65 D⁽⁷⁾.

Discussion

Pauling, Gordy and Saylor⁽¹⁾ explained the long C—Cl bond length by assuming a resonance structure $Cl-CH_2=C=C^+-H$, but the present result clearly shows that it is unnecessary to consider such a resonance structure. The C—Cl bond was found to be a normal value of 1.780 Å. In addition to this, the resonance structure given above predicts a small quadrupole coupling constant and a large dipole moment. These are not found in the present data either. Laurie and Lide observed the C—Cl bond length in 1-chloro-2-butyne to be

TABLE VIII. COMPARISON OF MOLECULAR STRUCTURES

	Propargyl chloride $CH_2ClC\equiv CH$	Methyl chloride CH_3Cl	Ethyl chloride CH_3CH_2Cl
C—Cl (Å)	1.780ᵃ⁾	1.781ᵇ⁾	1.7785ᵉ⁾
C—C (Å)	1.465ᵃ⁾	—	1.5495ᵉ⁾
χ_{bond} (Cl^{35}) (Mc./sec.)	−75.8ᵃ⁾	−74.740ᶜ⁾	−70.07ᵉ⁾
μ (D)	1.68ᵃ⁾	1.869ᵈ⁾	2.05ᶠ⁾

a) The present paper.
b) S. L. Miller, L. C. Aamodt, G. Dousmanis, C. H. Townes and J. Kraitchman, *J. Chem. Phys.*, **20**, 1112 (1952).
c) S. Geschwind, R. Gunther-Mohr and C. H. Townes, *Phys. Rev.*, **81**, 288 (1951).
d) R. G. Shulman, C. H. Townes and B. P. Dailey, ibid., **78**, 145 (1950).
e) R. S. Wagner and B. P. Dailey, *J. Chem. Phys.*, **26**, 1588 (1957).
f) C. P. Smyth, "Dielectric Behavior and Structure" McGraw-Hill Book Co., New York, N. Y. (1955), p. 269.

1.79_8 Å[18]. The data were, however, not sufficiently accurate and in addition the presence of internal rotation complicated the problem.

It is of some help to compare the constants of the propargyl chloride molecules with those of some other molecules. Table VIII shows such a comparison, where methyl and ethyl chlorides are taken as reference substances.

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[18] V. W. Laurie and D. R. Lide, Jr., ibid., 31, 939 (1959).