Microwave Spectrum of Propargyl Halides. II. Molecular Structure and Second-Order Quadrupole Effect of Propargyl Bromide

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In the previous papes[1] the C—Cl distance in propargyl chloride was reported to be close to the usual C-Cl bond length, 1.780±0.002 Å. The determination of the C—Br length in propargyl bromide is also of interest to obtain an additional assurance to the conclusion obtained in the previous paper.

An anomaly due to accidental degeneracy in rotational energy has been observed in bromine nuclear quadrupole hyperfine structure of some b-type Q-branch transitions[2]. The deviation from the first-order theory amounted to several megacycles. An analysis using the second-order perturbation has enabled us to know the direction of the principal axes and principal values of the quadrupole coupling constant of the bromine atom. It was found that the direction of the largest principal value of the coupling constants coincided with that of the C—Br bond and the asymmetry parameter was very small*.

1) E. Hirota and Y. Morino, This Bulletin, 34, 341 (1961).
2) Preliminary account is given in the paper, Y. Kikuchi, E. Hirota and Y. Morino, *J. Chem. Phys.*, 31, 1139 (1959).
* Recently the microwave spectrum of ethyl iodide was measured by Kasuya and Oka[3]. They found a hyperfine structure of the iodine atom deviating from the first-order theory.
3) T. Kasuya and T. Oka, *J. Phys. Soc., Japan*, 15, 296 (1960).

Experimental

The spectra of propargyl bromide, $CH_2{}^{79}BrC{\equiv}CH$, $CH_2{}^{81}BrC{\equiv}CH$, $CH_2{}^{79}BrC{\equiv}CD$ and $CH_2{}^{81}BrC{\equiv}CD$, were observed by a Stark modulation spectrometer described in the previous paper. The two isotopic species of bromine have almost equal natural abundance, hence no special preparation was necessary. The deuterated samples were obtained by the method used for the preparation of deuterated propargyl chloride.

Results

Rotational Spectra and Rotational Constants. —Propargyl bromide is also a nearly prolate symmetric top, similar to the chloride. The symmetry plane includes a- and b-axes, hence a- as well as b-type transitions are expected to be observed.

Table I gives the observed center frequencies. Preliminary assignment is based on frequencies expected for the assumed structure and hyperfine patterns. Transitions of a-type R-branch, $J_{1,J} \rightarrow J+1_{1,J+1}$, split into four lines and are easily identified by their characteristic hyperfine structures. The assignment of b-type Q-branch transitions is confirmed by plotting the asymmetry parameter b_P versus the quantity $A-(B+C)/2$.

The rotational constants and the asymmetry

TABLE I. OBSERVED AND CALCULATED CENTER FREQUENCIES (Mc./sec.)

Transition	$CH_2{}^{79}BrC{\equiv}CH$		$CH_2{}^{81}BrC{\equiv}CH$		$CH_2{}^{79}BrC{\equiv}CD$		$CH_2{}^{81}BrC{\equiv}CD$	
	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.
a-Type								
$6_{0,6}\rightarrow 7_{0,7}$	29035.53	29035.59	28843.44	28843.46	27359.91	27359.92	27178.13	27178.01
$6_{1,6}\rightarrow 7_{1,7}$	28460.66	28460.76	28275.01	28274.95	26820.29	26820.65	26644.31	26644.52
$6_{1,5}\rightarrow 7_{1,6}$	29721.56	29721.58	29520.15	29520.46		28001.53	27811.32	27811.37
$6_{2,5}\rightarrow 7_{2,6}$	29099.90	29099.97	28906.35	28906.25	27419.44	27419.53	27235.99	27236.07
$6_{2,4}\rightarrow 7_{2,5}$	29171.76	29171.81	28976.40	28976.40	27485.36	27485.50	27301.11	27300.52
$5_{0,5}\rightarrow 6_{0,6}$	24903.78	24904.57	24739.83	24739.50		23466.94		23310.34
$5_{1,5}\rightarrow 6_{1,6}$	24399.30	24399.29	24240.00	24239.93	22993.25	22993.14	22841.84	22841.79
$5_{1,4}\rightarrow 6_{1,5}$	25479.55	25480.30	25308.40	25307.79		24005.60		23842.20
$4_{1,4}\rightarrow 5_{1,5}$	20335.98	20335.82	20203.04	20202.97	19163.99	19163.81		19037.41
$3_{1,3}\rightarrow 4_{1,4}$	16270.72	16270.71	16164.26	16164.38	15332.75	15332.94	15231.60	15231.63
b-Type								
$13_{0,13}\rightarrow 13_{1,12}$	28406.9	28414.0	28270.2	28275.0	26945.4	26945.9	26815.7	26816.0
$12_{0,12}\rightarrow 12_{1,11}$	26906.93	26911.78	26791.33	26794.45	25545.00	25545.56	25435.05	25435.40
$11_{0,11}\rightarrow 11_{1,10}$	25563.6	25566.2	25466.9	25468.0	24290.1	24290.0	24197.6	24197.4
$10_{0,10}\rightarrow 10_{1,9}$	24367.0	24368.6	24286.7	24287.3	23171.6	23171.9	23095.0	23094.6
$9_{0,9}\rightarrow 9_{1,8}$	23309.9	23310.7	23243.9	23243.9	22184.3	22183.7	22120.1	22119.7
$8_{0,8}\rightarrow 8_{1,7}$	22384.6	22384.2	22330.7	22330.0	21318.0	21317.9	21265.6	21265.4
$7_{0,7}\rightarrow 7_{1,6}$	21578.3	21581.5	21538.3	21538.0				
$6_{0,6}\rightarrow 6_{1,5}$	20896.0	20895.5	20861.7	20861.0				
$5_{0,5}\rightarrow 5_{1,4}$	20319.5	20319.8	20292.9	20292.7				
$9_{1,9}\rightarrow 10_{0,10}$	26159.13	26164.36	25854.17	25860.54				

TABLE II. ROTATIONAL CONSTANTS, ASYMMETRY PARAMETERS, AND CENTRIFUGAL DISTORTION CONSTANTS

		$CH_2{}^{79}BrC{\equiv}CH$	$CH_2{}^{81}BrC{\equiv}CH$	$CH_2{}^{79}BrC{\equiv}CD$	$CH_2{}^{81}BrC{\equiv}CD$
A	obs.	21010.0±3 Mc./sec.	20986.5±3 Mc./sec.	20045.8±3 Mc./sec.	20021.0±3 Mc./sec.
	calcd.	21012.0	20987.9	20047.3	20022
B	obs.	2169.31±0.2	2154.37±0.2	2043.49±0.2	2029.28±0.2
	calcd.	2169.41	2154.51	2043.06	2028.96
C	obs.	1989.09±0.2	1976.34±0.2	1874.70±0.2	1862.50±0.2
	calcd.	1989.19	1976.44	1874.36	1862.27
	b_P	-4.7600×10^{-3}	-4.7045×10^{-3}	-4.6662×10^{-3}	-4.6136×10^{-3}
	D_J	0.001 Mc./sec.	0.001 Mc./sec.	0.001 Mc./sec.	~0 Mc./sec.
	D_{JK}	−0.0455	−0.0432	−0.0505	−0.0460

TABLE III. THE HYDROGEN TO HYDROGEN DISTANCE IN METHYLENE GROUP (Å)

	$CH_2{}^{79}BrC{\equiv}CH$	$CH_2{}^{81}BrC{\equiv}CH$	$CH_2{}^{79}BrC{\equiv}CD$	$CH_2{}^{81}BrC{\equiv}CD$
r(H···H)	1.7098	1.7108	1.7092	1.7084

parameters are given in Table II, and the frequencies calculated by using these constants are compared with the observed ones in Table I. A rough correction is made for the centrifugal distortion by assuming the expression $-D_J J^2(J+1)^2 - D_{JK} J(J+1) K_{-1}^2$. The observed values of D_J and D_{JK} are given in Table II.

Structure Analysis.—The number of structural parameters is the same as that of the chloride. Again the H···H distance in methylene group is given by

$$r(\mathrm{H\cdots H}) = [(I_a + I_b - I_c)/m_{\mathrm{H}}]^{1/2} \qquad (1)$$

The values for the four isotopic species given in Table III are close to each other, their average being 1.7096 Å. The eight constants are left to calculate other structural parameters. Since the mass ratio of two bromine isotopes ^{79}Br and ^{81}Br is almost equal to unity and the bromine atom is located so close to the a-axis, the data are not sufficient to calculate seven parameters. The following values are assumed: methylene C—H is equal to 1.090 Å, ∠CCH to 111°30′, C≡C to 1.207 Å, and acetylene C—H to 1.060 Å. The acetylene C—H and C—D bond lengths are assumed to be equal. The linearity of the group C—C≡C—H is again assumed. By means of the method of least-squares the

bond lengths C—Br and C—C and the bond angle CCBr are found to be 1.9415 Å, 1.4549 Å, and 111°59′, respectively.

Thus far, the effect of inertia defect is ignored, but, as mentioned in the previous paper, the results given above for the three parameters do not change appreciably even by taking account of the inertia defect. In addition, since the weight of a bromine atom is more than twice as great as that of a chlorine atom, errors in the parameters C—Br and ∠CCBr may be small. The results are given in Table IV.

TABLE IV. MOLECULAR STRUCTURE

C—Br	1.9415 Å	H···H*	1.7096 Å
C—C	1.4549 Å	∠CCBr	111°59′

Assumed values

C—H (methylene) 1.090 Å

C—H, C—D (acethylene) 1.060 Å

C≡C	1.207 Å	∠CCH	111°30′

* Correction for the inertia defect is not made.

Second-Order Quadrupole Effect. — Theory[4] indicates that the quadrupole energy is expressed as follows, averaging over rotational states of an asymmetric molecule

$$E_Q=(IJ\tau F|H_Q|IJ\tau F)+\sum_{J'\tau'}\frac{|(IJ\tau F|H_Q|IJ'\tau'F)|^2}{E_{J\tau}-E_{J'\tau'}} \quad (2)$$

Usually the difference in rotational energies $E_{J\tau}-E_{J'\tau'}$, is much larger than the quadrupole energy hence the second terms may be omitted. For a nearly prolate symmetric top the first-order energy

$$(IJ\tau F|H_Q|IJ\tau F)=\frac{1}{J(J+1)}\{\chi_{aa}[3K_{-1}^2-J(J+1)-3\sum_n(n-1)C_nb_P^n-\sum_n nC_nb_P^{n-1}]-2\chi_{bb}\sum_n nC_nb_P^{n-1}\}\cdot f(IJF) \quad (3)$$

is a good approximation for the quadrupole energy, where $\chi_{ff}=eQ\partial^2V/\partial f^2$, $f=a$, b and c are molecule-fixed axes chosen as the principal axes of inertia, and $f(IJF)$ is Casimir's function. However, if rotational energies $E_{J\tau}$ and $E_{J'\tau'}$ are almost degenerate, the second-order terms can not be ignored. The matrix elements have been derived by Bragg[5]:

$$(IJ\tau F|H_Q|IJ+A\tau'F)=g_a(IJF)(J\tau M_J=J|\chi_{ZZ}|J+A\tau'M_J=J) \quad (4)$$

where $\chi_{ZZ}=eQ\partial^2V/\partial Z^2$ (Z is a space-fixed axis), $\alpha=0, \pm1, \pm2$, and

$$g_0=[3C(C+1)-4I(I+1)J(J+1)]\div[8I(2I-1)J(2J-1)] \quad (5a)$$

$$g_1=[F(F+1)-I(I+1)-J(J+2)]\times[(I+J+F+2)(I-J+F)\times(J-I+F+1)(J+I-F+1)]^{1/2}\div\{8I(2I-1)J[(2J+1)]^{1/2}\} \quad (5b)$$

$$g_2=[(I+J+F+2)(I+J+F+3)(I-J+F-1)\times(I-J+F)(J-I+F+1)(J-I+F+2)\times(I+J-F+1)(I+J-F+2)]^{1/2}\div\{16I(2I-1)[(2J+1)(J+1)]^{1/2}\} \quad (5c)$$

where $C=F(F+1)-I(I+1)-J(J+1)$. The $(J|J-1)$ and $(J|J-2)$ elements may be determined from equations given above by the Hermitian property of H_Q. The tensor component χ_{ZZ} is expressed in terms of direction cosines Φ_{Zf} and χ_{aa}, etc., the components of eQq tensor referred to the principal axes a, b and c. The result is

$$\chi_{ZZ}=(\Phi_{Za}^2-\Phi_{Zc}^2)\chi_{aa}+(\Phi_{Zb}^2-\Phi_{Zc}^2)\chi_{bb}+2\Phi_{Za}\Phi_{Zb}\chi_{ab}+2\Phi_{Zb}\Phi_{Zc}\chi_{bc}+2\Phi_{Zc}\Phi_{Za}\chi_{ca} \quad (6)$$

The asymmetric top wave functions as well as direction cosines belong to the representation of the four group[6]. Thus the matrix element of χ_{ZZ} is zero unless the direct product of the representation of the two rotational states is equal to that of $\Phi_{Zf}\,\Phi_{Zf'}$. Table V gives the symmetry of the direction cosines and the wave functions.

The rotational wave function for a slightly asymmetric top molecule is approximately given by

$$\Psi_K^{(1)}=S_K+\alpha S_{K-2}+\beta S_{K+2} \quad (7)$$

where S_K is Wang's symmetric top wave function, and the coefficients α and β are given by Lide[7]. For propargyl bromide the wave function of this type is sufficient to calculate the second-order quadrupole energy, since the asymmetry parameter of the molecule is small.

Transitions of b-type Q-branches are observed to split into four lines by the quadrupole effect of bromine nucleus. For transitions of high J the first-order theory predicts that the splitting $\nu_4-\nu_3$ is equal to $\nu_2-\nu_1$, but the deviation was observed, in particular, for the transition $12_{0,12}\rightarrow12_{1,11}$ (Table VI).

In applying the second-order theory described above the energies of the states which couple with the states $12_{0,12}$ and $12_{1,11}$ are first calculated. The result is shown in Tables VII

4) See, for example, M. W. P. Strandberg, "Microwave Spectroscopy", Methuen & Co., Ltd., London (1954), Chapter IV.

5) J. K. Bragg, *Phys. Rev.*, **74**, 533 (1948). See also G. Racah, ibid., **62**, 438 (1942).

6) G. W. King, R. M. Hainer and P. C. Cross, *J. Chem. Phys.*, **11**, 27 (1943).

7) D. R. Lide, Jr., ibid., **20**, 1761 (1952).

TABLE V. SYMMETRY OF DIRECTION COSINES AND WAVE FUNCTIONS

Direction cosine	K_{-1}	K_1		E	C_2^a	C_2^b	C_2^c
Φ_{Za}^2, Φ_{Zb}^2, Φ_{Zc}^2	e	e	A	1	1	1	1
$\Phi_{Zc}\Phi_{Zb}$, Φ_{Za}	e	o	B_a	1	1	−1	−1
$\Phi_{Zc}\Phi_{Za}$, Φ_{Zb}	o	o	B_b	1	−1	1	−1
$\Phi_{Za}\Phi_{Zb}$, Φ_{Zc}	o	e	B_c	1	−1	−1	1

TABLE VI. LINE SEPARATIONS OF HYPERFINE STRUCTURES OF b-TYPE Q-BRANCH LINES

Transition	$CH_2{}^{79}BrC{\equiv}CH$			$CH_2{}^{81}BrC{\equiv}CH$			$CH_2{}^{79}BrC{\equiv}CD$			$CH_2{}^{81}BrC{\equiv}CD$		
	$\nu_2-\nu_1$	$\nu_3-\nu_2$	$\nu_4-\nu_3$	$\nu_2-\nu_1$	$\nu_3-\nu_2$	$\nu_4-\nu_3$	$\nu_2-\nu_1$	$\nu_3-\nu_2$	$\nu_4-\nu_3$	$\nu_2-\nu_1$	$\nu_3-\nu_2$	$\nu_4-\nu_3$
$13_{0,13}\rightarrow13_{1,12}$	4.14	41.43	6.99	3.30	35.04	5.40	3.71	43.70	7.69	3.04	36.60	6.09
$12_{0,12}\rightarrow12_{1,11}$	10.47	40.59	~0	6.81	33.48	1.71	8.55	42.58	2.42	6.25	35.15	2.80
$11_{0,11}\rightarrow11_{1,10}$	6.51	38.97	4.98	5.52	32.37	4.29	6.87	40.80	5.21	5.59	33.88	4.50
$10_{0,10}\rightarrow10_{1,9}$	6.51	37.95	5.58	5.52	31.23	4.86	7.06	39.36	6.54	5.76	33.34	4.82
$9_{0,9}\rightarrow9_{1,8}$	7.32	36.36	6.51	5.76	30.39	5.37	7.74	38.38	6.86	6.21	31.42	5.84
$8_{0,8}\rightarrow8_{1,7}$	7.65	35.28	7.29	6.72	29.49	6.24	8.29	36.83	8.09	6.94	31.03	6.49
$7_{0,7}\rightarrow7_{1,6}$	4.89	40.74	2.37	4.35	34.74	2.10						
$6_{0,6}\rightarrow6_{1,5}$	9.99	34.05	8.49	8.46	28.26	7.65						
$5_{0,5}\rightarrow5_{1,4}$	16.08			13.9	28.0							

TABLE VII. STATES COUPLING WITH $12_{0,12}$ AND THEIR ENERGY DIFFERENCES IN Mc./sec.

State	$E(12_{0,12})-E(J'\tau')$			
	$CH_2{}^{79}BrC{\equiv}CH$	$CH_2{}^{81}BrC{\equiv}CH$	$CH_2{}^{79}BrC{\equiv}CD$	$CH_2{}^{81}BrC{\equiv}CD$
$10_{0,10}$	95006.7	94384.4	89533.3	88939.3
$10_{2,8}$	18110.3	17554.3	16109.0	15586.0
$11_{2,10}$	−26955.9	−27223.1	−26370.1	−26616.9
$12_{2,10}$	−78067.2	−77973.8	−74500.4	−74405.1
$13_{2,12}$	−130783.8	−130361.7	−124203.3	−123792.9
$14_{0,14}$	−111267.7	−110542.5	−104862.6	−104170.4
$14_{2,12}$	−191185.0	−190324.8	−181064.9	−180239.9
$10_{1,10}$	80545.6	79884.1	75641.6	75014.2
$11_{1,10}$	23982.4	23756.1	22405.3	22188.0
$12_{1,12}$	−12875.3	−12928.3	−12397.7	12444.1
$13_{1,12}$	−82010.7	−81522.4	−77457.7	−76994.7
$14_{1,14}$	−122480.5	−121820.7	−115690.4	−115056.0

TABLE VIII. STATES COUPLING WITH $12_{1,11}$ AND THEIR ENERGY DIFFERENCES IN Mc./sec.

State	$E(12_{1,11})-E(J'\tau')$			
	$CH_2{}^{79}BrC{\equiv}CH$	$CH_2{}^{81}BrC{\equiv}CH$	$CH_2{}^{79}BrC{\equiv}CD$	$CH_2{}^{81}BrC{\equiv}CD$
$10_{1,9}$	97547.1	96888.9	91904.6	91277.9
$10_{3,7}$	−49195.1	−49830.0	−48378.4	−48962.1
$11_{1,11}$	62763.7	62276.3	59067.8	58608.9
$11_{3,9}$	−94962.1	−95291.8	−91501.1	−91794.0
$12_{3,9}$	−144934.8	−144930.2	−138584.9	−138559.3
$13_{3,13}$	−38752.5	−38579.1	−36601.2	−36429.1
$13_{1,11}$	−199018.7	−198653.7	−189544.5	−189175.5
$14_{1,13}$	−114429.1	−113658.5	−107812.3	−107078.5
$14_{3,11}$	−257371.4	−256614.8	−244522.1	−243780.1
$10_{2,9}$	45646.4	44958.5	42227.2	41581.5
$11_{0,11}$	76446.2	76005.1	72226.3	71807.5
$11_{2,9}$	−962.0	−1324.9	−1668.2	−2005.4
$12_{2,11}$	−49895.0	−49948.2	−47797.5	−47838.1
$13_{0,13}$	−26703.6	−26470.8	−24983.3	−24758.8
$13_{2,11}$	−105599.8	−105254.7	−100246.0	−99909.3
$14_{2,13}$	−162004.1	−161313.4	−153434.4	−152765.8

TABKE IX. HYPERFINE STRUCTURES OF a-TYPE R-BRANCH LINES (Mc./sec.)

$J''\tau''\rightarrow J'\tau'$	$F''\rightarrow F'$	$CH_2{}^{79}BrC\equiv CH$		$CH_2{}^{81}BrC\equiv CH$		$CH_2{}^{79}BrC\equiv CD$		$CH_2{}^{81}BrC\equiv CD$	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
$6_{1,6}-7_{1,7}$	15/2−17/2	−1.99	−2.00	−1.63	−1.52	−0.91	−1.76	−1.63	−1.59
	13/2−15/2	−0.29	−0.26	−0.24	−0.22	−0.30	−0.19	−0.26	−0.16
	9/2−11/2	+1.26	+1.11	+1.03	+0.90	+1.23	+1.10	+1.05	+0.98
	11/2−13/2	+2.95	+3.04	+2.42	+2.31	+2.84	+2.70	+2.43	+2.30
$5_{1,5}-6_{1,6}$	13/2−15/2	−2.65	−2.59	−2.17	−2.17	−2.54	−2.54	−2.17	−2.10
	11/2−13/2	−0.15	−0.19	−0.12	−0.10	−0.16	−0.08	−0.15	−0.12
	7/2− 9/2	+1.65	+1.62	+1.36	+1.30	+1.62	+1.55	+1.39	+1.34
	9/2−11/2	+4.15	+4.12	+3.40	+3.43	+4.00	+3.97	+3.41	+3.37
$4_{1,4}-5_{1,5}$	11/2−13/2	−3.76	−3.76	−3.08	−3.08	−3.61	−3.64	−3.08	
	9/2−11/2	+0.40	+0.31	+0.32	+0.31	+0.34	+0.11	+0.28	
	5/2− 7/2	+2.13	+2.32	+1.75	+1.80	+2.11	+2.01	+1.81	
	7/2− 9/2	+6.28	+6.11	+5.15	+5.14	+6.05	+6.41	+5.17	
$3_{1,3}-4_{1,4}$	9/2−11/2	−5.80	−5.72	−4.76	−4.90	−5.57	−5.55	−4.75	−4.76
	7/2− 9/2	+2.25	+2.26	+1.84	+1.87	+2.09	+2.23	+1.76	+1.90
	3/2− 5/2	+2.38		+1.95		+2.41		+2.08	
	5/2− 7/2	+10.43	+10.37	+8.55	+8.84	+10.06	+10.18	+8.59	+8.60

TABLE X. HYPERFINE STRUCTURES OF $12_{0,12}\rightarrow 12_{1,11}$ TRANSITION (Mc./sec.)

$J''\rightarrow J'$	$F''\rightarrow F'$	$CH_2{}^{79}BrC\equiv CH$		$CH_2{}^{81}BrC\equiv CH$		$CH_2{}^{79}BrC\equiv CD$		$CH_2{}^{81}BrC\equiv CD$	
		Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd·	Obs.
$12_{0,12}-12_{1,11}$	27/2−27/2	−30.54	−30.71	−23.50	−23.53	−29.92	−29.85	−23.71	−23.80
	25/2−25/2	−20.43	−20.24	−16.67	−16.72	−21.39	−21.30	−17.43	−17.55
	29/2−29/2	+20.39	+20.35	+16.71	+16.76	+21.36	+21.28	+17.47	+17.60
	23/2−23/2	+20.34	+20.35	+18.43	+18.47	+23.77	+23.70	+20.30	+20.40

TABLE XI. QUADRUPOLE COUPLING CONSTANTS OF THE BROMINE ATOM

	$CH_2{}^{79}BrC\equiv CH$	$CH_2{}^{81}BrC\equiv CH$	$CH_2{}^{79}BrC\equiv CD$	$CH_2{}^{81}BrC\equiv CD$
χ_{aa}	316 Mc./sec.	259 Mc./sec.	300 Mc./sec.	255 Mc./sec.
χ_{bb}	−16	−13	−8	−5
χ_{cc}	403	336	415	342
χ_{xx}	−286	−238	−295	−241
χ_{yy}	−301	−246	−292	−250
χ_{zz}	587	484	587	491
θ	33°48′	33°59′	34°49′	34°36′
θ'	34° 2′	33°58′	35° 7′	35° 3′
η	0.03	0.02	−0.01	0.02

TABLE XII. COMPARISON OF THE MOLECULAR CONSTANTS

Compound	r(C—Br)	eQ_q	
		^{79}Br	^{81}Br
Propargyl bromide	1.9415 Å	587 Mc./sec.	484 Mc./sec.
Methyl bromide	1.939 Å*	577.3**	482.4**
Ethyl bromide	1.9400 Å***	416.5***	349.1***

* J. W. Simmons and W. E. Anderson, *Phys. Rev.*, **80**, 338 (1950).
** A. H. Sharbaugh and J. Mattern, ibid., **75**, 1102 (1949).
*** R. S. Wagner, B. P. Dailey and N. Solimene, *J. Chem. Phys.*, **26**, 1593 (1957).

and VIII where the states are chosen by symmetry consideration.

It is to be noted that the state $11_{2,9}$ is nearly degenerate with the state $12_{1,11}$, while the energies of other states differ by more than 10000 Mc./sec. from that of the state $12_{0,12}$ or $12_{1,11}$. Since the symmetry of the state $11_{2,9}$ is B_a and that of the state $12_{1,11}$ B_b while that of $\Phi_{Za}\Phi_{Zb}$ is B_c as is given in Table V, the state $11_{2,9}$ couples with the state $12_{1,11}$ by the quadrupole Hamiltonian of the form $\Phi_{Za}\Phi_{Zb}\chi_{ab}$. This coupling is dominant in the second-order terms, thus the second-order energy is nearly proportional to $\chi_{ab}{}^2$. The other terms χ_{bc} and

χ_{ca} are equal to zero by the symmetry of the molecule.

The line separations given in Table VI, $\nu_2-\nu_1$ and $\nu_4-\nu_3$, are expressed as

$$\nu_2-\nu_1=K\chi_{aa}+L\chi_{bb}+M\chi_{ab}^2 + (\text{small terms involving } \chi_{aa}^2,\ \chi_{bb}^2 \text{ and } \chi_{aa}\chi_{bb}) \quad (8a)$$

$$\nu_4-\nu_3=K\chi_{aa}+L\chi_{bb}+N\chi_{ab}^2 + (\text{small terms involving } \chi_{aa}^2,\ \chi_{bb}^2 \text{ and } \chi_{aa}\chi_{bb}) \quad (8b)$$

where K, L, M and N are constants. In these expressions the first two terms are the first-order energies and the others are the second-order energies. It is to be noted that the first two terms are the same for both equations. In employing Eq. 7 the second-order terms of δ in the coefficients, α and β, are neglected. After appropriate correction is made for the last term, χ_{ab} is obtained by subtracting Eq. 8b from Eq. 8a. By substituting the value of χ_{ab} into Eq. 8a or 8b, a linear equation of χ_{aa} and χ_{bb} is obtained. Another linear relation is given by well-resolved a-type R-branch transitions (Table IX), for which the second-order effect seems to be small. From these relations χ_{aa} and χ_{bb} are calculated. The results are compared with the observed ones in Tables IX and XI.

By use of χ_{aa}, χ_{bb} and χ_{ab} the principal values of the χ-tensor and the directions of the principal axes (x, y and z) are determined without any assumptions. The θ designates the angle between the a- and z-axes and the θ' that between the direction of the C—Br bond and the a-axis. The two angles are found to agree within experimental errors. The asymmetry parameter η, which is given by $(\chi_{xx}-\chi_{yy})/\chi_{zz}$, is close to zero for the four isotopic species, where the x-axis is taken in the (ab) plane. The average value of η is $+0.015\pm0.013$.

Discussion

The C—Br bond length obtained, 1.9415 $\pm$0.005 Å, is close to the values usually observed in saturated hydrocarbon bromides. Table XII shows comparison of this value with those of methyl and ethyl bromides. It is to be noted that the values for the C—Br length in those three compounds are of the same order of magnitude within experimental errors.

The z-direction of the quadrupole coupling constant coincides with the direction of the C—Br bond within errors involved in the present experiment. It is a good confirmation of the current assumption usually made. The value of χ_{zz} is compared with those of methyl and ethyl bromides in Table XII. The three values of the coupling constant are also close to each other.

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