

Microwave Spectrum of BrCN and Dependence of Quadrupole Coupling Constant on the Vibrational State

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(Received April 8, 1957)

The hyperfine structure of the $J=1\leftarrow 0$ and $J=2\leftarrow 1$ rotational transitions of BrCN has been measured. The values of $eqQ(\text{Br}^{79})$ and $eqQ(\text{Br}^{81})$ for each vibrational state were obtained as follows.

	Vibrational State (v_1, v_2, v_3)	From the frequencies of the $J=1\leftarrow 0$ transition	From the frequencies of the $J=2\leftarrow 1$ transition
$eqQ(\text{Br}^{79})$ in Mc/sec	(0, 0, 0)	685.6 ± 0.4	685.3 ± 0.8
	(1, 0, 0)	687.9 ± 0.6	689.1 ± 0.7
	(0, 2 ⁰ , 0)	681.6 ± 0.7	680.2 ± 0.9
$eqQ(\text{Br}^{81})$ in Mc/sec	(0, 0, 0)	572.8 ± 0.2	572.7 ± 0.6
	(1, 0, 0)	576.1 ± 0.9	574.2 ± 0.7
	(0, 2 ⁰ , 0)	568.9 ± 1.5	567.3 ± 1.5

Considerable increase of eqQ for the stretching vibration ($v_1=1$) is explained in terms of the decrease of the double bond character of Br-C bond, and the decrease of eqQ for the excitation of the bending vibration ($v_2=1$) is ascribed to the variation of the z component of q tensor.

§ 1. Introduction

The measurement of the quadrupole hyperfine structure of the spectrum of pure rotational transitions in a simple molecule gives the quadrupole coupling constant with considerable accuracy. As is well known, molecules in different vibrational states have different rotational constants, and if the microwave spectrum of a molecule in the excited vibrational state is measurable, it gives the quadrupole coupling constants in the excited vibrational states.

Tetenbaum and Javan measured the hyperfine structure of the $J=6\leftarrow 5$ transition of BrCN and the $J=4\leftarrow 3$ transition of ICN, respectively, and found the variation of eqQ with the excitation of the bending vibration^{1,2}. The hyperfine components of the $J=1\leftarrow 0$ and the $J=2\leftarrow 1$ transitions of ICN molecule in the (0, 0, 0), (1, 0, 0) and (0, 2⁰, 0) vibrational states were reported by the present authors, and the variation of eqQ was found to come not only from the excitation of the bending vibration but also from the excitation of the stretching vibration³. Lower J transitions are more appropriate for this type of investigation.

In the present paper, the results of the measurement of the hyperfine components of the $J=1\leftarrow 0$ and the $J=2\leftarrow 1$ transitions of

BrCN are described. The three vibrational frequencies of BrCN are $\nu_1=580\text{ cm}^{-1}$, $\nu_2=368\text{ cm}^{-1}$ and $\nu_3=2187\text{ cm}^{-1}$. The microwave spectrum of the molecule in the (0, 0, 0), (1, 0, 0) and (0, 2, 0) states were observed but the study of the molecule in (0, 1, 0) states was given up as they show the complicated Stark behavior of the I -type doublets.

§ 2. Experiments and Results

The measured frequencies are listed in Tables I, II, III and IV. The errors of the observed frequencies mainly come from the weakness of the lines and from the hyperfine splittings due to the quadrupole moment of N^{14} . The errors are expected to be less than 0.1 Mc/sec for almost all lines.

From these measured frequencies, the rotational constant B and the quadrupole coupling constant eqQ in each vibrational state were derived by means of the least square fit to the formula

$$\nu = 2(J+1)B + Y(F)eqQ + Z(F)(eqQ)^2/B.$$

Some lines with large experimental errors were not used in the analysis. In addition to the hyperfine structures due to the quadrupole moment of Br, some lines show further splittings due to the quadrupole moment of N^{14} . From these splittings, $eqQ(\text{N}^{14})$ in BrCN is

Table I. Frequencies of the hyperfine components of the $J=1\leftarrow 0$ rotational transition of Br^{79}CN molecule in Mc/sec.

F_1 F_1	F_2	F_f F_1	F_2	observed	calculated	calculated absorption coefficient in cm^{-1}
(0, 0, 0) lines						
3/2,	5/2	5/2,	7/2	8206.92	8207.05	2.7×10^{-6}
3/2,	5/2	5/2,	5/2	8206.18	8206.24	
3/2,	5/2	5/2,	3/2	8207.39	8207.40	
3/2,	3/2	3/2,	5/2	8377.95	8377.91	1.9×10^{-6}
3/2,	3/2	3/2,	3/2	8378.58	8378.53	
3/2,	3/2	3/2,	1/2	8379.38	8379.31	
3/2		1/2		8070.45	8070.43	0.9×10^{-6}
(1, 0, 0) lines						
3/2		5/2		8183.87	8183.97	1.7×10^{-7}
3/2		3/2		8356.48	8356.38	1.2×10^{-7}
3/2		1/2		8047.08	8047.08	0.6×10^{-7}
(0, 2 ^o , 0) lines						
3/2		5/2		8245.29	8245.39	8.0×10^{-8}
3/2		3/2		8416.30	8216.22	5.7×10^{-8}
3/2		1/2		8109.78	8109.75	2.8×10^{-8}

Table II. Frequencies of the hyperfine components of the $J=2\leftarrow 1$ rotational transition of Br^{81}CN molecule in Mc/sec.

F_1 F_1	F_2	F_f F_1	F_2	observed	calculated	calculated absorption coefficient in cm^{-1}
(0, 0, 0) lines						
3/2,	5/2	5/2,	7/2	8165.68	8165.74	2.5×10^{-6}
3/2,	5/2	5/2,	5/2	8164.96	8164.93	
3/2,	3/2	3/2,	5/2	8308.27	8308.27	1.8×10^{-6}
3/2,	3/2	3/2,	3/2	8308.89	8308.89	
3/2,	3/2	3/2,	1/2	8309.67	8309.67	
3/2		1/2		8051.48	8051.47	0.8×10^{-6}
(1, 0, 0) lines						
3/2		5/2		8142.89	8142.74	1.5×10^{-7}
3/2		3/2		8286.87	8286.95	1.1×10^{-7}
3/2		1/2		8028.04	8028.11	0.5×10^{-7}
(0, 2 ^o , 0) lines						
3/2		3/2		8346.07	8346.07	5.2×10^{-8}
3/2		1/2		8090.25	8090.25	2.4×10^{-8}

Table III. Frequencies of the hyperfine components of the $J=2\leftarrow 1$ rotational transition of Br^{79}CN molecule in Mc/sec.

F_1 F_1	F_2	F_f F_1	F_2	observed	calculated	calculated absorption coefficient in cm^{-1}
(0, 0, 0) lines						
5/2		7/2		16466.35	16466.64	27×10^{-6}
3/2		5/2				
5/2		5/2		16638.40	16638.19	4.0×10^{-6}
5/2		3/2		16517.8	16517.25	0.4×10^{-6}
3/2,	5/2	3/2,	5/2	16345.38	16345.35	4.6×10^{-6}
3/2,	3/2	3/2,	3/2	16346.17	16346.10	
3/2,	5/2	1/2,	3/2	16172.90	16172.82	0.7×10^{-6}
3/2,	3/2	1/2,	3/2	16172.30	16172.20	
3/2,	1/2	1/2,	3/2	16173.40	16173.60	
1/2		3/2		16653.58	16653.62	3.7×10^{-6}
1/2		1/2		16480.92	16481.11	3.6×10^{-6}

F_i F_1	F_2	F_f F_1	F_2	observed	calculated	calculated absorption coefficient in cm^{-1}
(1, 0, 0) lines						
5/2		7/2		16420.97	16420.91	17×10^{-7}
3/2		5/2				
5/2		5/2		16593.38	16593.40	2.5×10^{-7}
3/2		3/2		16299.07	16299.10	2.8×10^{-7}
1/2		3/2		16608.6	16608.93	2.3×10^{-7}
1/2		1/2		16435.3	16435.46	2.2×10^{-7}
(0, 2 ⁰ , 0) lines						
5/2		7/2		16542.45	16542.38	8.0×10^{-7}
3/2		5/2				
5/2		5/2		16712.9	16712.64	1.2×10^{-7}
1/2		3/2		16727.97	16727.96	1.1×10^{-7}
1/2		1/2		16556.67	16556.75	1.1×10^{-7}

Table IV. Frequencies of the hyperfine components of the $J=2 \leftarrow 1$ rotational transition of Br^{81}CN molecule in Mc/sec.

F_i F_1	F_2	F_f F_1	F_2	observed	calculated	calculated absorption coefficient in cm^{-1}
(0, 0, 0) lines						
5/2		7/2		16375.43	16375.18	25×10^{-6}
3/2		5/2				
5/2		5/2		16518.62	16518.52	3.6×10^{-6}
5/2		3/2		16417.0	16417.25	0.4×10^{-6}
3/2, 5/2	3/2, 5/2	3/2, 5/2	3/2, 5/2	16273.00	16272.99	4.4×10^{-6}
3/2, 3/2	3/2, 1/2	3/2, 3/2	3/2, 3/2	16273.62	16273.61	
3/2, 1/2		3/2, 3/2		16274.38	16274.39	
3/2		1/2		16129.96	16129.75	0.7×10^{-6}
1/2		3/2		16531.31	16531.32	3.5×10^{-6}
1/2		1/2		16387.20	16387.30	3.4×10^{-6}
(1, 0, 0) lines						
5/2		7/2		16329.72	16329.55	15×10^{-7}
3/2		5/2				
5/2		5/2		16473.20	15473.25	2.2×10^{-7}
3/2		3/2		16227.73	16227.88	2.7×10^{-7}
1/2		3/2		16486.04	16486.09	2.2×10^{-7}
(0, 2 ¹ , 0) lines						
5/2		7/2		16451.27	16451.27	7.5×10^{-7}
3/2		5/2				
1/2		3/2		16605.92	16605.92	1.1×10^{-7}

calculated by means of Bardeen and Townes's theory⁴). The values of quadrupole coupling

constants and the rotational constants are listed in Tables V and VI, respectively.

Table V. Values of $\text{eqQ}(\text{Br}^{79})$, $\text{eqQ}(\text{Br}^{81})$ and $\text{eqQ}(\text{N}^{14})$ in Mc/sec.

Vibrational State	Transition	$\text{eqQ}(\text{Br}^{79})$	$\text{eqQ}(\text{Br}^{81})$
(0, 0, 0)	$\{J=1 \leftarrow 0$	685.6 ± 0.4	572.8 ± 0.2
	$\{J=2 \leftarrow 1$	685.3 ± 0.8	572.7 ± 0.6
(1, 0, 0)	$\{J=1 \leftarrow 0$	687.9 ± 0.6	576.1 ± 0.9
	$\{J=2 \leftarrow 1$	689.1 ± 0.7	574.2 ± 0.7
(0, 2 ¹ , 0)	$\{J=1 \leftarrow 0$	681.6 ± 0.7	568.9 ± 1.5
	$\{J=2 \leftarrow 1$	681.2 ± 0.9	567.3 ± 1.5

Table VI. Values of rotational constants used in the calculation of the frequencies in Mc/sec.

Vibrational State	Transition	Br^{79}CN	Br^{81}CN
(0, 0, 0)	$\{J=1 \leftarrow 0$	4120.32	4096.92
	$\{J=2 \leftarrow 1$	4120.278	4096.825
(1, 0, 0)	$\{J=1 \leftarrow 0$	4108.93	4085.74
	$\{J=2 \leftarrow 1$	4108.864	4085.425
(0, 2 ¹ , 0)	$\{J=1 \leftarrow 0$	4139.49	4115.83
	$\{J=2 \leftarrow 1$	4139.189	4115.820

$$\text{eqQ}(\text{N}^{14}) = -3.89 \text{ Mc/sec.}$$

§ 3. Discussions

From Table V it is seen that eqQ increases when the stretching vibration is excited. This is reasonable in view of the variation of the double bond character of Br-C bond. When the stretching vibration is excited, Br-C bond is elongated owing to the anharmonicity of the potential, and the double bond character of the Br-C bond decreases, and thus eqQ increases. The elongation of the bond is calculated from the variation of the moment of inertia of the molecule with the vibrational excitation. Since ν_1 vibration is concerned mainly with the stretching of the Br-C bond, C-N distance may be assumed to be constant. Accordingly, the elongation of the Br-C bond is calculated to be

$$\delta R = (M_{\text{Br}} + M_{\text{C}} + M_{\text{N}})(I' - I) / 2M_{\text{Br}}[M_{\text{C}}l_1 + M_{\text{N}}(l_1 + l_2)],$$

where M_{Br} , M_{C} , M_{N} are the masses of Br, C and N atoms, l_1 and l_2 are the bond lengths of Br-C and C-N bonds in the ground vibrational state, and I' and I are the moments of inertia of the molecule in the (1, 0, 0) and the (0, 0, 0) states, respectively. I' is calculated from the values of B_v obtained by Tetenbaum taking into account the effect of Fermi resonance¹⁾. Substituting $l_1 = 1.789 \text{ \AA}$, $l_2 = 1.160 \text{ \AA}$ ⁵⁾ and $I' - I = 0.465 \text{ a.m.u. \AA}^2$, δR was calculated to be 0.0049 \text{ \AA} both for Br⁷⁹CN and Br⁸¹CN. It was reported in the preceding paper that the variation of q is given by the formula³⁾

$$\frac{q + \delta q}{q} = 1 + \frac{[\frac{1}{2} - \varepsilon(\frac{1}{2} - s + d)]x(2x + 1)}{[-(1 - s + d)(1 - x) - (\frac{1}{2} - s + d)(1 + \varepsilon)x]} \cdot \frac{\delta R}{(R - R_1)}.$$

Using the values $s - d = 0.15^6)$, $\varepsilon = 0.15^6)$, $x = 0.15^6)$ and $\delta R = 0.0049$, it is found that

$$(q + \delta q)/q = 1.0044.$$

This is in fair agreement with the experimental values of $(\text{eqQ})_{v_1-1}/(\text{eqQ})_0$ listed in Table VII.

Table VII. Values of $(\text{eqQ})_v/(\text{eqQ})_0$

		Transition (1, 0, 0) (0, 2 ⁰ , 0)	
observed	Br ⁷⁹ CN	$\begin{cases} J=1 \leftarrow 0 \\ J=2 \leftarrow 1 \end{cases}$	1.0034 0.9942
			1.0055 0.9924
	Br ⁸¹ CN	$\begin{cases} J=1 \leftarrow 0 \\ J=2 \leftarrow 1 \end{cases}$	1.0058 0.9905
			1.0026 0.9932
calculated			1.0044 0.9910

It is seen from Table V that eqQ decreases when the bending vibration is excited. This decrease is expressed by the formula²⁾,

$$q_v = (1 - 3\bar{\theta}^2/2)q_0.$$

In the case of BrCN, $1 - 3\bar{\theta}^2/2$ is calculated to be 0.9910, using the data from the vibrational analysis. This should be compared with the experimental values of $(\text{eqQ})_{v_2-2}/(\text{eqQ})_0$ listed in Table VII.

§ 4. Acknowledgement

The authors are indebted to Prof. K. Shimoda for his kind guidance and encouragement during the course of this investigation. They are also grateful to Prof. Y. Morino of the Department of Chemistry for his continued interest in this work.

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