Interatomic Distances and Nuclear Quadrupole Couplings in ClCN, BrCN, and ICN*

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(Received May 10, 1948)

The following nuclear and molecular constants have been obtained from microwave measurements of the pure rotational spectra of ClCN ($J=2\rightarrow3$ transition), BrCN ($J=3\rightarrow4$), and ICN ($J=4\rightarrow5$). The moments of inertia from the ground vibrational states are, in g-cm^2 $\times10^{-40}$: for $Cl^{35}C^{12}N^{14}$, 140.5_{11}; for $Cl^{35}C^{13}N^{14}$, 141.2_{45}; for $Cl^{37}C^{12}N^{14}$, 143.4_{80}; for $Cl^{37}C^{13}N^{14}$, 144.2_{83}; for $Br^{79}C^{12}N^{14}$, 203.6_{21}; for $Br^{81}C^{12}N^{14}$, 204.7_{86}; for $Br^{79}C^{13}N^{14}$, 205.9_{64}; for $Br^{81}C^{13}N^{14}$, 207.1_{72}; for $I^{127}C^{12}N^{14}$, 260.0_{99}; and for $I^{127}C^{13}N^{14}$, 264.0_{72}. The interatomic distances in A for the ground vibrational states are $d_{CCl}=1.630$, $d_{CN}=1.163$, for ClCN; $d_{CBr}=1.789$, $d_{CN}=1.160$, for BrCN; and $d_{CI}=1.995$, $d_{CN}=1.159$, for ICN. Quadrupole couplings in mc/s evaluated from the hyperfine structure are: for Cl^{35}, -83.5; for Cl^{37}, -65.0; for Br^{79}, 686; for Br^{81}, 573; and for I^{127}, -2420.

THE microwave absorption of BrCN and ClCN caused by pure rotation of the molecules ($J=2\rightarrow3$ for BrCN for $J=1\rightarrow2$ for ClCN) was first reported by Townes, Holden, and Merritt.[1] The observed complex spectra were subsequently explained by Bardeen and the above authors[2] as a splitting in the rotational levels caused by nuclear quadrupole moments of the halides and of nitrogen. Rotational transitions of ICN ($J=4\rightarrow5$) and BrCN ($J=3\rightarrow4$) have been observed by Gordy, Smith, Smith, and Ring.[3] With increased precision of measurement, certain anomalies have been observed in these spectra,[4,5] which have been explained[5] as second-order interactions between levels of the same F and M_F but of different J.

In the earlier publications no accurate values for the interatomic distances have been given, and for ICN, since only one isotope was observed, it was necessary to assume the CN distance in

order to obtain an estimate of the IC length. By observations on samples containing C^{13} isotope enriched to 15 percent and by frequency mea-

TABLE I. Hyperfine structure of the $J=3\rightarrow4$ rotational transition of cyanogen bromide, ground vibrational state.

Transition $F \rightarrow F'$	Frequency, mc/s Observed	Calculated*	Relative intensity Observed	Theoretical
Br^{79}C^{12}N^{14}				
$eqQ=686$	$\nu_0=32,961.79$ mc/s			
$9/2\rightarrow11/2$	32,956.68	32,956.66	176	100
$7/2\rightarrow 9/2$	32,956.68	32,956.78		76.4
$5/2\rightarrow 7/2$	32,976.40	32,976.28	88	57.4
$3/2\rightarrow 5/2$	32,976.40	32,976.48		42.9
$5/2\rightarrow 5/2$	32,804.56	32,804.56	9	6.9
Br^{79}C^{13}N^{14}				
$eqQ=686$	$\nu_0=32,586.84$ mc/s			
$9/2\rightarrow11/2$	32,581.73	32,581.71	176	100
$7/2\rightarrow 9/2$	32,581.73	32,581.84		76.4
$5/2\rightarrow 7/2$	32,601.46	32,601.33	88	57.4
$3/2\rightarrow 5/2$	32,601.46	32,601.53		42.9
Br^{81}C^{12}N^{14}				
$eqQ=573$	$\nu_0=32,774.38$ mc/s			
$9/2\rightarrow11/2$	32,770.13	32,770.09	176	100
$7/2\rightarrow 9/2$	32,770.13	32,770.18		76.4
$5/2\rightarrow 7/2$	32,786.65	32,786.51	88	57.4
$3/2\rightarrow 5/2$	32,786.65	32,786.66		42.9
$9/2\rightarrow 9/2$	32,913.24	32,913.52	5	6.9
$7/2\rightarrow 7/2$	32,720.28	32,720.29	9	9.1
$5/2\rightarrow 5/2$	32,643.13	32,643.10	5	6.9
Br^{81}C^{13}N^{14}				
$eqQ=573$	$\nu_0=32,396.85$ mc/s			
$9/2\rightarrow11/2$	32,392.59	32,392.56	176	100
$7/2\rightarrow 9/2$	32,392.59	32,392.65		76.4
$5/2\rightarrow 7/2$	32,409.06	32,408.98	88	57.4
$3/2\rightarrow 5/2$	32,409.06	32,409.12		42.9

* First- and second-order theories (references 2, 5) are both employed in calculating the nuclear interactions of the halogen. The nuclear interactions of the nitrogen are neglected.

[1] C. H. Townes, A. N. Holden, and F. R. Merritt, Phys. Rev. 71, 64 (1947).

[2] C. H. Townes, A. N. Holden, J. Bardeen, and F. R. Merritt, Phys. Rev. 71, 664 (1947); J. Bardeen and C. H. Townes, ibid. 73, 97 (1948).

[3] W. Gordy, W. V. Smith, A. G. Smith, and H. Ring, Phys. Rev. 72, 259 (1947).

[4] O. R. Gilliam, H. D. Edwards, and W. Gordy, Phys. Rev. 73, 635 (1948).

[5] J. Bardeen and C. H. Townes, Phys. Rev. 73, 627 (1948).

TABLE II. Hyperfine structure of the $J=4\rightarrow5$ rotational transition of cyanogen iodide, ground vibrational state.

Transition $F\rightarrow F'$	Frequency, mc/s Observed	Calculated*	Relative intensity Observed	Theoretical
		$I^{127}C^{12}N^{14}$		
$eqQ=-2420$	$\nu_0=32{,}255.55$ mc/s			
$13/2\rightarrow15/2$	32,268.33	32,268.32	100	100
$11/2\rightarrow13/2$	32,278.55	32,278.45	69	80.8
$9/2\rightarrow11/2$	32,248.52	32,248.48	63	64.3
$7/2\rightarrow 9/2$	32,215.56	32,215.66	54	50.6
$5/2\rightarrow 7/2$	32,203.57	32,203.61	45	39.3
$3/2\rightarrow 5/2$	32,226.85	32,226.80	30	30.6
$13/2\rightarrow13/2$	31,848.77	31,848.80	15	6.7
$11/2\rightarrow11/2$	32,200.58	32,200.62	21	10.4
$9/2\rightarrow 9/2$	32,386.29	32,386.35	15	11.5
		$I^{127}C^{13}N^{14}$		
$eqQ=-2420$	$\nu_0=31{,}770.35$ mc/s			
$13/2\rightarrow15/2$	31,783.31	31,783.12	100	100
$11/2\rightarrow13/2$	31,793.46	31,793.30	90	80.8
$9/2\rightarrow11/2$	31,763.34	31,763.27	60	64.3
$7/2\rightarrow 9/2$	31,730.50	31,730.55	45	50.6
$5/2\rightarrow 7/2$	31,718.28	31,718.41	30	39.3
$3/2\rightarrow 5/2$	31,741.50	31,741.70	21	30.6

* First- and second-order theories (references 2, 5) are both employed in calculating the nuclear interactions of the halogen. The nuclear interactions of the nitrogen are neglected.

surements of increased accuracy[6] made with harmonics of a 10 mc signal monitored by WWV, we have been able to make unambiguous and accurate determinations of the structures of these molecules. In addition, determinations of certain of the nuclear quadrupole couplings have been obtained which are more accurate than those previously reported.

In Tables I and II are given the calculated and observed hyperfine structures of BrCN ($J=3\rightarrow4$ transition) and ICN ($J=4\rightarrow5$ transition) which are caused by the halogen nuclei. The much smaller nuclear coupling of the nitrogen causes a further splitting of these lines which becomes evident at very low pressures. These nitrogen effects were not investigated since the nitrogen nuclear coupling in each of these molecules has been carefully determined in other recent work.[3, 7] The second-order theory of Bardeen and Townes[5] has been used with the first-order theory in calculating the positions of the BrCN and ICN lines, and in determining the nuclear quadrupole couplings of the bromine and the iodine. In the calculated hyperfine structure of ClCN ($J=2\rightarrow3$

[6] Method to be described in a later publication by R. Unterberger and W. V. Smith.
[7] A. G. Smith, H. Ring, W. V. Smith, and W. Gordy, Phys. Rev. 73, 633 (1948).

TABLE III. Hyperfine structure of the $J=2\rightarrow3$ rotational transition of cyanogen chloride, ground vibrational state.

Transition $F\rightarrow F'$	Frequency, mc/s Observed	Calculated	Relative intensity Observed	Theoretical
		$Cl^{35}C^{12}N^{14}$		
$eqQ=-83.5$	$\nu_0=35{,}824.94$ mc/s			
$7/2\rightarrow9/2$ $5/2\rightarrow7/2$	35,825.95	35,825.95	169	{100 68.6
$3/2\rightarrow5/2$ $1/2\rightarrow3/2$	35,820.65	35,820.80	68	{44.8 28.0
$7/2\rightarrow7/2$	35,805.09	35,805.05	15	11.4
$5/2\rightarrow5/2$	35,835.74	35,835.75	21	14.6
		$Cl^{35}C^{13}N^{14}$		
$eqQ=-83.5$	$\nu_0=35{,}638.77$ mc/s			
$7/2\rightarrow9/2$ $5/2\rightarrow7/2$	35,639.78	35,639.78	169	{100 68.6
$3/2\rightarrow5/2$ $1/2\rightarrow3/2$	35,634.85	35,634.63	62	{44.8 28.0
$7/2\rightarrow7/2$	35,618.81	35,618.88	21	11.4
$5/2\rightarrow5/2$	35,649.56	35,649.58	21	14.6
		$Cl^{37}C^{12}N^{14}$		
$eqQ=-65.0$	$\nu_0=35{,}083.46$			
$7/2\rightarrow9/2$ $5/2\rightarrow7/2$	35,084.15	35,084.25	169	{100 68.6
$3/2\rightarrow5/2$ $1/2\rightarrow3/2$	35,080.39	35,080.24	53	{44.8 28.0
$7/2\rightarrow7/2$	35,067.99	35,067.97	21	11.4
$5/2\rightarrow5/2$	35,091.97	35,091.89	21	14.6
		$Cl^{37}C^{13}N^{14}$		
$eqQ=-65.0$	$\nu_0=34{,}888.26$			
$7/2\rightarrow9/2$	34,889.05	34,889.05		

* First-order theory only (reference 2) is employed in calculating the nuclear interaction of the halogen. The nuclear interaction of the nitrogen is taken into account in computing the center of gravity of the line.

transition), shown in Table III, the second-order effects are neglected since they are within the range of experimental error. However, the N as well as the Cl nuclear quadrupole coupling is

TABLE IV. Nuclear quadrupole couplings in the cyanogen halides.

Molecule	Isotope	$eQ(\partial^2 V/\partial z^2)$
ClCN	Cl^{35}	-83.5[a]
	Cl^{37}	-65.0[a]
	N^{14}	-3.67[b]
BrCN	Br^{79}	686[a]
	Br^{81}	573[a]
	N^{14}	-3.82[c]
ICN	I^{127}	-2420[a]
	N^{14}	-3.80[d]

[a] Values determined in present work. The coupling for I^{127} is identical with that recently obtained by Bardeen and Townes, reference 5.
[b] C. H. Townes et al, reference 2.
[c] C. H. Townes, privately communicated.
[d] A. G. Smith, et al, reference 7.

TABLE V. Frequencies ν_0 of hypothetical unsplit rotational lines and resulting moments of inertia of cyanogen halides in the ground vibrational state.

Molecule	J transition	ν_0(mc/s)	$I_B(10^{-40}$ g-cm$^2)$
Cl^{35}C^{12}N^{14}	2→3	35,824.94	140.5107*
Cl^{35}C^{13}N^{14}		35,638.77	141.2448
Cl^{37}C^{12}N^{14}		35,083.46	143.4804
Cl^{37}C^{13}N^{14}		34,888.26	144.2832
Br^{79}C^{12}N^{14}	3→4	32,961.79	203.6212
Br^{81}C^{12}N^{14}		32,774.38	204.7856
Br^{79}C^{13}N^{14}		32,586.84	205.9641
Br^{81}C^{13}N^{14}		32,396.85	207.1720
I^{127}C^{12}N^{14}	4→5	32,255.55	260.0994
I^{127}C^{13}N^{14}		31,770.35	264.0717

* Because Planck's constant is known to four places only, the last three figures given in the moment of inertia values have only relative significance.

here taken into account. The most noticeable effect of the N coupling is to split the $F=3/2$ →5/2 and 3/2→3/2 lines so that the latter is too weak to detect and the frequency determination of the former is less accurate than it is for the rest of the lines.

In Table IV are listed the values of the halogen nuclear quadrupole couplings determined here and the previously determined values for nitrogen. The ratio of the quadrupole moment of Br^{79} to that of Br^{81} is here determined as 1.197 and that of Cl^{35} to Cl^{37} as 1.274. These ratios compare favorably with the values 1.197 and 1.273 found in a similar manner from CH$_3$Br and CH$_3$Cl respectively.[8]

Table V gives the moments of inertia which were calculated from the spectral data, while in Table VI are shown the internuclear distances obtained. In calculating these distances from the moments of inertia it is assumed that the internuclear distances in the ground vibrational state are the same for a given molecule containing different isotopes. Though not strictly true, the assumption probably does not introduce an error

[8] W. Gordy, J. W. Simmons, and A. G. Smith, Phys. Rev. 73, 243 (1948).

TABLE VI. Molecular dimensions of the cyanogen halides in the ground vibrational state.

Molecule	CN distance (A)	CX distance (A)	Reference
ClCN	1.163	1.630	a, d
BrCN	1.160	·1.789	b, d
ICN	1.159	1.995	c, d

ª Using M_X for Cl^{35} =34.9800 a.m.u. and M_X for Cl^{37} =36.9775 a.m.u. as given by F. W. Aston, Proc. Roy. Soc. A163, 391 (1937).
ᵇ Using M_X for Br^{79} =78.9417 a.m.u. and M_X for Br^{81} =80.9400 a.m.u. as given by F. W. Aston, Nature 141, 1096 (1938).
ᶜ Using M_X for I^{127} =126.932 a.m.u. as given by F. W. Aston, Proc. Roy. Soc. A115, 487 (1927).
ᵈ Other constants used: h =6.624×10^{-27} erg-sec., mass of atom of unit atomic mass =1.6599×10^{-24} g, and M_C for C^{12} =12.00386 a.m.u., all as given by R. T. Birge, Rev. Mod. Phys. 13, 233 (1941); M_C for C^{13} =13.0074 a.m.u. as given by an average of M. L. E. Oliphant, Nature 137, 396, 407 (1936), and J. D. Cockcroft and W. B. Lewis, Proc. Roy. Soc. A49, 883 (1936), M_N =14.0075 as given by M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. 9, 373 (1937).

in the third figure. The various atomic weights and other constants used in the calculations are listed in the tables.

The carbon to halogen internuclear distances in these halogen cyanides are appreciably shorter than those found for the corresponding distances in the methyl halides.[8] This pronounced effect, which was detectable in the earlier less accurate measurements, may be attributed largely to resonance between the electronic structures $X^+ = C = N^-$ and $X - C \equiv N$ which gives the XC bond some double bond character. This type of resonance would also reduce the bond order of the CN, and one would therefore expect a somewhat longer CN bond length than that for a normal CN triple bond. This expected lengthening of the CN bond, which should be much less pronounced than the shortening of the XC bond,[9,10] is revealed for the first time in the measurements reported here. The added triple bond radii[11] of C and N, 1.149A, are definitely shorter than the CN lengths listed in Table VI.

[9] L. Pauling, Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1939), p. 164.
[10] R. S. Mulliken, C. A. Rieke, and W. G. Brown, J. Am. Chem. Soc. 63, 41 (1941).
[11] L. Pauling, reference 9, p. 154.