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Letters to the Editor

Publication of brief reports of important discoveries in physics may be secured by addressing them to this department. The closing date for this department is, for the issue of the 1st of the month, the 8th of the preceding month and for the issue of the 15th, the 23rd of the preceding month. No proof will be sent to the authors. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents. Communications should not exceed 600 words in length.

Rotational Spectra of Some Linear Molecules near 1-cm Wave-Length

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ROTATIONAL spectra of several linear molecules have been found in the region near 1-cm wave-length. The lines are observed on an oscilloscope on which frequency is plotted against variation in absorption. Absorption takes place in a 4-meter length of wave guide containing a few tenths of one mm Hg pressure of the absorbing gas. The technique is similar to that already described.[1]

In some cases there are a number of weaker lines accompanying the main rotational line. The measured frequencies and relative intensities are given in Table I. For the stronger lines frequency measurements have a probable error of about two megacycles, although frequency differences are somewhat more accurate. Relative intensities are not highly accurate, particularly for the weakest lines. The ClCN lines at 23,885 and 23,389 mc appear to be caused by $Cl^{35}CN$ and $Cl^{37}CN$ molecules, respectively, which are in the ground vibrational state and undergo a transition from $J=1$ to $J=2$. Similarly the BrCN lines at 24,713 and 24,570 mc are attributed to molecules of $Br^{79}CN$ and $Br^{81}CN$, respectively, in the ground vibrational state which make a transition from $J=2$ to $J=3$. The single OCS line is caused by the rotational transition $J=1$ to $J=2$. With these lines and assignments, and with no corrections for vibrations in the ground state, the moments of inertia are as in Table II. Using the isotopic frequency shift in ClCN, the CN distance is calculated to be 1.15A. The isotopic shift in BrCN is also consistent with this value, but does not allow a very accurate determination of the CN distance. Assuming the CN distances in BrCN and ClCN are the same, we obtain the values for the internuclear distances given in Table III.

Table I. Measured frequencies and intensities of lines in rotational spectra near one cm wave-length.

	Frequency in megacycles	Intensity relative to strongest line
BrCN	24,468	.05
	24,506	.15
	24,570	1.00
	24,576	.1
	24,608	.4
	24,619	.1
	24,631	.1
	24,645	.1
	24,658	.1
	24,683	.1
	24,713	1.0
	24,754	.4
	24,759	.1
	24,780	.1
	24,799	.1
	24,824	.1
	24,884	.05
ClCN	23,373	.1
	23,389	.3
	23,401	.05
	23,862	.15
	23,864	.15
	23,885	1.00
	23,901	.15
OCS	24,325	

Table II. Computed moments of inertia.

Molecule	Moment of inertia ($g\ cm^2 \times 10^{-40}$)
$Br^{79}CN$	203.64
$Br^{81}CN$	204.83
$Cl^{35}CN$	140.47
$Cl^{37}CN$	143.45
OCS	137.93

Table III. Internuclear distances.

Bond	Bond distance	Bond distance from electron diffraction[2]
C−N	1.15A	1.13±0.04A
Br−C	1.79	1.79±0.02
Cl−C	1.64	1.67±0.02

The C−N distance determination is very sensitive to small changes in the isotopic shift. Until a satisfactory explanation of the subsidiary lines is obtained which will at the same time give assurance that no unknown effects are contributing to the isotopic shift, the internuclear distances given above must be regarded as tentative.

The data can be used to distinguish between different possible structures for these molecules. The moments of inertia determined here and the electron diffraction data are consistent with the structures Cl−C−N and Br−C−N, but not with Cl−N−C and Br−N−C which have sometimes been proposed.[3] If one assumes an arrangement Cl−N−C and takes 1.09A (the smallest reasonable value from electron diffraction data) as the N−C distance, the above value for the moment of inertia gives a total length for the molecule of 2.86A. This is in distinct disagreement with the electron diffraction value for the total length 2.80±0.02A. From the above table it may be seen that the spectroscopic data give, assuming the Cl−C−N arrangement, a total molecular length 2.79A which is in good agreement with electron diffraction results. Similarly Br−C−N gives a total length 2.94A as compared with the electron diffraction value 2.92±0.02A, but if the Br−N−C structure is assumed the total length of the molecule cannot be less than 3.01A.

The frequency of the OCS line is in agreement with that recently reported by Dakin, Good, and Coles.[4]

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[1] C. H. Townes, Phys. Rev. **70**, 665 (1946).

[2] J. Y. Beach and A. Turkevich, J. Am. Chem. Soc. **61**, 299 (1939).

[3] For a discussion see Sidgwick, *Organic Chemistry of Nitrogen* (Oxford University Press, New York, 1937), p. 326.

[4] T. W. Dakin, W. E. Good, and D. K. Coles, Phys. Rev. **70**, 560 (1946).