TABLE I. Observed transitions and frequencies $J=0\leftrightarrow 1$.

$v=0$	$\mathrm{Br^{79}F}$	$\mathrm{Br^{81}F}$
F 3/2–1/2	20,985.5 mc/sec.	20,928.4 mc/sec.
3/2–5/2	21,202.6	21,110.4
3/2–3/2	21,475.4	21,337.5
$v=1$		
F 3/2–1/2	20,828.9 mc/sec.	20,772.3 mc/sec.
3/2–5/2	21,045.6	20,954.6
3/2–3/2	21,319.4	21,181.7

TABLE II. Molecular constants of BrF.

	$\mathrm{Br^{79}F}$	$\mathrm{Br^{81}F}$
B_e	$10{,}706.9_5$ mc/sec.	10,655.7
I_e	$78.355(10)^{-40}$ g cm^2	$78.658(10)^{-40}$
α	156.3 mc/sec.	155.8 mc/sec.
r_e	$1.759(10)^{-8}$ cm	
μ	1.29 debye units	
eqQ	+1089.0 mc/sec.	+909.2

in this dihalide are to be noted. The most convincing evidence that this spectrum is due to BrF is obtained when the ratio of B_e values derived from the spectrum 0.995213, is compared with that computed from the mass measurements of the bromine isotopes[3] 0.995207.

While the fit of the triplets to the conventional quadrupole coupling expression, including second-order corrections, was not entirely satisfactory, the precision of the frequency measurements did not appear to justify the evaluation of the magnetic coupling factor, as was done for the dihalide FCl by Gilbert, Roberts, and Griswold.[4]

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* This document is based on work performed under contract for the AEC by Carbide and Carbon Chemicals Corporation, at Oak Ridge, Tennessee.

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Intensity Distribution of the Second Positive ($C^3\Pi\rightarrow B^3\Pi$) Band System of Molecular Nitrogen

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RECENT interest shown in the intensity distributions of the vibrational band-systems of molecular nitrogen radiated from auroral displays, and from the night sky[1] prompts this brief account of some calculations of the intensity distributions of the second positive band system, made in connection with an experimental investigation being undertaken here of the kinetics of excitation of the energy levels of molecular nitrogen in gaseous electrical discharge.

The integrated intensity of a molecular band may be written:

$$I(v',v'')=CN(v')E^4(v',v'')p(v',v''),\tag{1}$$

where $N(v')$ is the population of molecules in the v' vibrational level of the upper electronic state concerned in the transition, $E(v',v'')$ is the energy radiated in the transition between v' and v'', v'' is the vibrational level in the lower electronic state upon which the transition ends, and

$$p(v',v'')=\left|\int_{-\infty}^{\infty}\psi(v')M\psi(v'')dx\right|^2,$$

where $\psi(v')$ and $\psi(v'')$ are the respective wave functions of the levels v' and v'', x is the internuclear separation, and M is the dipole moment of the molecule. p is a fractional transition probability as $\Sigma_{v''}\,p(v',v'')=1$ for each v'. C is a constant of proportionality.

Following a method suggested and used first by Pearse and Gaydon,[2] and later used by Miss Pillow,[3] we have calculated the values of $p(v',v'')$ by numerical integration of the wave-function product, for all the observed bands of the second positive system of nitrogen under the same conditions of simplifying approximation as are used in references 2 and 3. Briefly, these are (a) treating M as constant, and (b) linearly distorting the Hermite polynomial forms of $\psi(v')$ and $\psi(v'')$ expected for a harmonic oscillator, to fit the empirical, yet experimentally justified Morse curves for the $C^3\Pi$ and $B^3\Pi$ states of nitrogen.

These values of $p(v',v'')$ are shown in Table I. Table II shows the values of $E^4(v',v'')p(v',v'')$ adjusted to a value of 100 at the (0, 0) band. It will be evident from Eq. (1) that the values of Table II, when compared with measured intensities will yield information relating to the population $N(v')$ of the upper level concerned in the transition, and therefore to the probable major mechanism responsible for the excitation of the level.

TABLE I. $p(v',v'')$.

$v' \backslash v''$	0	1	2	3	4	5	6	7	8	9	10
0	0.53	0.27	0.12	0.05	0.02	0.01					
1	0.43	0.04	0.21	0.12	0.08	0.07	0.05	0.00			
2	0.21	0.39	0.01	0.10	0.08	0.07	0.08	0.05	0.00_3		
3	0.01	0.37	0.26	0.02	0.03	0.06	0.07	0.10	0.08	0.00	
4	—	0.04	0.45	0.16	0.08	0.01	0.04	0.04	0.08	0.09	0.01

TABLE II. $p(v',v'')E^4(v',v'')$.

$v' \backslash v''$	0	1	2	3	4	5	6	7	8	9	10
0	100	40	14	4.8	1.3	0.39					
1	110	8.9	32	14	7.7	5.3	2.7	0.01			
2	67	99	1.6	17	11	7.2	6.2	2.9	0.15		
3	3.1	120	67	4.5	5.9	7.4	7.6	8.4	5.1	0.00_5	
4	—	15	150	43	17	1.0	5.6	4.6	6.8	6.0	0.64

Similar calculations are being made for the other molecular nitrogen band systems and for the NOβ- and γ-systems in connection with the experimental work referred to above. The possible geometry of a three-dimensional representation of the Tables I and II is also being worked upon.

While these calculations were being made an interesting paper by Bates[1] appeared, in which some similar work was reported. However, as data for far fewer bands of the second positive system were reported there, it is thought worth while to present the above calculations.

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New Types of Microwave Transitions Involving *l*-Type Doubling in OCS and HCN*

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MICROWAVE measurements of the vibration-rotation interaction called *l*-type doubling are available for a number of linear XYZ molecules.[1] Two new types of transitions involving this interaction have been observed which confirm the expected

TABLE I. Observed lines in HCN and values of l-type doubling constant q.

J	Frequency in mc	q = frequency/$J(J+1)$ mc
6	9,460 ± 30	225.2 ± 0.8
8	16,147.67 ± 0.1	224.273 ± 0.002
10	24,689.96 ± 0.1	224.454 ± 0.001
11	29,650 ± 30	224.6 ± 0.3
12	35,043.24 ± 0.1	224.635 ± 0.001

functional dependence of l-type doubling on the vibrational and rotational quantum numbers.

For the $J=1\rightarrow 2$ transition of OCS, l-type doubling in the vibrational state $v_2=1$ produces a splitting of 25.34 mc. The corresponding doublets for the vibrational state $v_2=3$ have been found at 24,411±2 mc and 24,459±2 mc. Within experimental error, these show a separation just twice that of the $v_2=1$ state in accordance with the theory of Nielsen and Schaffer.[2]

A search of the HCN spectrum was made between 21,500 and 25,000 mc in an attempt to find the rotational spectrum of the dimer, $(HCN)_2$. Lines due to this dimer were expected under the conditions of search to have absorption coefficients several times greater than the minimum detectable value 5×10^{-9} cm^{-1}, but no lines due to $(HCN)_2$ were found. However, a line of intensity 3×10^{-6} cm^{-1} was found at 24,689.96 mc. The Stark components split from the above frequency according to the formula $\Delta\nu=AE^2M^2$, where E is the field strength and M the magnetic quantum number. This behavior and the number and relative intensities of Stark components showed clearly that the line corresponded to a $J=10$, $\Delta J=0$ transition. In order for the dimer $(HCN)_2$ to produce a line of the observed intensity it would have to be approximately 1 percent abundant at 10^{-2} mm Hg pressure. This appears impossible from previous measurements.[3] After checking carefully that the lines were not due to impurities, and after finding other similar lines with different values of J, the series of lines was identified as due to transitions directly between two l-type doublet states of the same J for HCN molecules in the first excited bending mode. The separation of such states should be $\nu=qJ(J+1)$, where q is the l-type doubling constant. Table I shows that frequencies of the five lines measured (some measured roughly with a wave meter, others accurately with a frequency standard) fit this formula very well. The values of q obtained from the accurately measured $J=8$, 10 and 12 lines of Table I show a systematic deviation proportional to J and of the order $q(B/\omega_2)$, which is to be expected in higher approximation. Extrapolating the values of q to $J=0$, one obtains $q=223.549$ mc.

TABLE II. Dipole moment of HCN in state $J=10$, $v_2=1$ from Stark displacement of $|M|=10$ component.

Displacement $\Delta\nu$ in mc	Square of field strength E^2(e.s.u./cm)^2	Dipole moment μ-debye units
54.48	411.93	2.943
60.4	455.31	2.949
61.65	454.07	2.980
		Average $\mu=2.957$

Stark effects for each of these lines show definitely the values of J listed in Table I and that $\Delta J=0$. The apparent lack of Stark displacement of the $M=0$ component is in agreement with expectations for the assigned transitions. A measurement of the molecular dipole moment was obtained for the state $v_2=1$, $J=10$, by measuring the Stark splitting $\Delta\nu$ of the $|M|=10$ component of the line at 24,689.96 mc. The results displayed in Table II give a dipole moment of 2.957±0.025 debye units. This is in good agreement with determinations by other methods[4] of the average dipole moment for gaseous HCN.

A further check on the identification of these HCN lines was obtained by comparison of intensities at 300°K and 195°K. Relative intensities agreed with the assumption that the lines were due to an excited molecule of energy $\omega_2=712$ cm^{-1} above the ground state.

The value $q=223.549$ mc is very different from the value 42 mc obtained from infra-red measurements.[5] However, it is supported by theoretical expectations. According to Nielsen,[6]

$$q=\frac{2B^2}{\omega_2}\Big[1+4\sum_{S'}\xi_{SS'}{}^2\lambda_S/(\lambda_{S'}-\lambda_S)\Big].$$

The term represented by a summation is somewhat difficult to evaluate. However, in the half-dozen other molecules for which l-type doubling has been measured, the first term $2B^2/\omega_2$ is less than the observed value of q by about 30 percent. For HCN, $2B^2/\omega_2=184.1$ mc, which is less than the measured value by a similar amount.

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MINUTES OF THE MEETING OF THE NEW ENGLAND SECTION AT WILLIAMS COLLEGE, WILLIAMSTOWN, MASSACHUSETTS, OCTOBER 22, 1949

THE thirty-third meeting of the New England Section of the American Physical Society was held at the Thompson Physical Laboratory, Williams College, Williamstown, Massachusetts on Saturday, October 22, 1949. Approximately one hundred members of this section were in attendance. The program included three invited papers, which formed a symposium on magnetism, and nine con-