

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

$v=0$	Br <sup>79</sup> F	Br <sup>81</sup> 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.

	Br <sup>79</sup> F	Br <sup>81</sup> F
$B_e$	10,706.9 <sub>4</sub> mc/sec.	10,655.7
$I_e$	78.355(10) <sup>-40</sup> g cm <sup>2</sup>	78.658(10) <sup>-40</sup>
$\alpha$	156.3 mc/sec.	155.8 mc/sec.
$r_e$	1.759(10) <sup>-8</sup> cm	
$\mu$	1.29 debye units	
$e\eta Q$	+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<sup>3</sup> 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.<sup>4</sup>

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

- <sup>1</sup> H. S. Booth and J. T. Pinkston, Chem. Rev. **41**, 421 (1947).  
<sup>2</sup> VanPeter Heinz Broderon and Hans Joachim Schumacher, Zeits. f. Naturforsch. **2a**, 358 (1947).  
<sup>3</sup> K. Ogata, Phys. Rev. **75**, 200 (1949).  
<sup>4</sup> Gilbert, Roberts, and Griswold, Phys. Rev. **76**, 1723 (1949).

## 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<sup>1</sup> 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:

$$I(v', v'') = CN(v')E^4(v', v'')p(v', v''), \quad (1)$$

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  $\sum_{v''} p(v', v'') = 1$  for each  $v'$ .  $C$  is a constant of proportionality.

Following a method suggested and used first by Pearse and Gaydon,<sup>2</sup> and later used by Miss Pillow,<sup>3</sup> 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

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 <sub>s</sub>		
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 <sub>s</sub>	
4	—	15	150	43	17	1.0	5.6	4.6	6.8	6.0	0.64

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.

Similar calculations are being made for the other molecular nitrogen band systems and for the  $NO\beta$ - and  $\gamma$ -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<sup>1</sup> 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.

<sup>1</sup> *The Emission Spectra of The Night Sky and Aurorae* (The Physical Society, London, 1948); D. R. Bates, Proc. Roy. Soc. **A196**, 217 (1949).

<sup>2</sup> R. W. B. Pearse and A. G. Gaydon, Proc. Roy. Soc. **A173**, 37 (1939).

<sup>3</sup> M. E. Pillow, Proc. Phys. Soc. London **62**, 237 (1949).

## 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.<sup>1</sup> Two new types of transitions involving this interaction have been observed which confirm the expected