level spacing for nuclei with $A \approx 100$ is a few volts, hence it should be a few millivolts for heavy nuclei. It is difficult to see why these should not capture slow neutrons very abundantly. The present considerations indicate how this difficulty may be removed. If the nuclear radius, or some equivalent parameter, were so adjusted that only the elements whose points lie high above the asymptotic curve in Fig. 4 possess a sufficiently large ρ to be strong neutron absorbers, there would be many elements of insufficient ρ interspersed between the absorbers.

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trons. It is interesting to note that experiments of W. L. Davidson, Jr., (unpublished), who determined the levels of Co^{60} and several other neighboring elements by deuteron bombardment, found spacings around 1.25 Mev in the neighborhood of $U \approx 3$ Mev. Theory would predict a ratio of about 400 for the spacings in cobalt at $U = 3$ Mev and 8 Mev, whereas the data cited yield about 40,000. Whether this discordance can be removed by supposing that the bombardment experiments yield only a small fraction of the total number of levels (cf. in this connection E. Pollard, Phys. Rev. **59**, 466 A (1941)) remains to be seen.

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Intensity Measurements in the Molecular Spectrum of Hydrogen

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Quantitative intensity measurements were made in the visible and infra-red of the H_2 spectrum for different conditions in the discharge tube. The present paper reports on the Fulcher bands. It appears that at the lower pressures no equilibrium exists and that therefore the concept of temperature has no meaning. By varying the pressure and current in the discharge tube the effective rotational temperature can be varied from 240°K to 1500°K. Whereas higher rotational states are favored with an increase in pressure, the higher vibrational states are suppressed, and this effect is largely independent of the current. From the behavior of the relative intensities with pressure and current density conclusions can be drawn regarding the elementary processes in the discharge. The results show that extreme care must be used when intensity measurements in band spectra are used for temperature measurements. Apart from the fact that the conditions in the discharge tube may be far from equilibrium, our results on the *P*- and *R*-branches show that the transition probabilities may be quite different, even in simple bands, from the values predicted by the elementary theory.

1. Introduction

The present paper gives some measurements of the changes in intensity of the lines of the Fulcher bands in hydrogen as the conditions in the discharge tube are varied, as the first part of a general survey of the intensities in the H_2 spectrum. The main purpose of the investigation was to relate these changes of intensity to the classification of the lines in the hope that the extension of such measurements to other lines would be helpful for the further analysis of the spectrum. We chose the Fulcher bands because of their relatively simple structure and the likelihood that by selecting particularly simple cases first we could get at least a qualitative picture of what happens in more complex cases. In carrying out these measurements we have adopted a reasonable compromise between high precision and extensiveness of the survey. We have taken all reasonable precautions to secure accuracy, but have made no effort to maintain the ultimate precision.

The first and only extensive quantitative intensity measurements were made by Ornstein, Kapuscinski and Eymers[1] and Kapuscinski and Eymers[2] on the stronger lines below 6441A.

As most of the stronger unclassified lines lie in the infra-red, it is very desirable to extend the measurements into the infra-red as far as possible, particularly since no quantitative intensity measurments of any kind exist beyond 6441A, and intensity estimates give no indication of the strength of the infra-red lines as compared to that of the visible lines.

However, the *changes* in the relative intensities

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[1] L. S. Ornstein, W. Kapuscinski and J. G. Eymers, Proc. Roy. Soc. **A119**, 83 (1928).

[2] W. Kapuscinski and J. G. Eymers, Proc. Roy. Soc. **A122**, 58 (1929).

of the lines when the conditions in the discharge tube are altered are of more significance for the classification of the lines than the intensities themselves. Previous measurements of such changes[3, 4] were all of a qualitative nature[5] and did not include the infra-red. Because the classification of the spectrum was then only imperfectly known, the nature of the observed changes could not be well ascertained. But even these qualitative observations have proved to be of great help in the classification of the H_2 spectrum.[4]

The study of the intensity distribution in a band system as a function of the conditions in the discharge tube proves a very effective and promising way for the analysis of the elementary processes in an electrical discharge. Some of our results are only tentative and should be checked by experiments especially designed for the particular purpose. The H_2 spectrum is particularly suited for such experiments, as several well-developed band systems occur with all bands perfectly resolved in a spectrograph of medium or even small size.

2. EXPERIMENTAL ARRANGEMENT

Spectrograph

For our measurements we chose a 15-foot concave grating spectrograph with a dispersion of 3.6A per mm. With this instrument the lines are satisfactorily resolved even when a wide slit (convenient for intensity measurements) is used. The astigmatism of the grating when corrected in the middle of the plate by a cylindrical lens between slit and grating, was small enough to be harmless over the portion of the plate actually used.

Discharge

The discharge tube, which was of the type used in this laboratory for wave-length measurements[6] was entirely of fused quartz and was water-cooled. The horizontal part was 42 cm long with an internal diameter of 5.5 mm and was viewed end on. Guided by the experience of others and by preliminary experiments, we carried out the measurements under the following five conditions:

SYMBOL	p	CURRENT	VOLTAGE SOURCE
L	0.06 mm	0.014 amp.	30,000-v spark coil
N	0.2	0.4	5,200-v transformer
H	20	0.4	13,500-v transformer
H′	20	0.04	13,500-v transformer
He	0.2 mm of H_2 in 150 mm of He		13,500-v transformer

The symbols L to He will be used throughout this paper to designate these types of discharge.

The pressures were measured when the tube was not in operation and are, therefore, directly proportional to the density of the gas. To reduce the dead volume, the tube, during operation, was shut off from the McLeod gauge and pump. Nevertheless that volume was not negligible and the densities during operation are slightly less than those corresponding to the given pressures.

Calibration of the plates

Intensity marks were applied to the plates in much the same way as by Ornstein, Kapuscinski and Eymers. The light from a tungsten filament fell on a step slit with six openings of from 0.169 to 4.08 mm width, and produced continuous spectra, the intensity of which was proportional to the width of the respective slits. These spectra were, of course, on the same plate as the H_2 spectrum and had the same exposure time. The intensity of the standard lamp was cut down when necessary by means of a rotating sector with two openings, the speed being adjusted to interrupt the light about 120 times per second, which is also the frequency of the light in the hydrogen discharge. These continuous spectra were photometered[7] about every 20 mm on each plate to obtain the calibration curves.

The standard tungsten lamp used for most of the work originated in the laboratory of the N. V. Philips Gloeilampenfabriek in Eindhoven, Holland, and was calibrated by Dr. W. de Groot in 1929, so that the intensity distribution as function of the wave-length was known. This enabled us to correct for the variations of the

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[3] T. R. Merton and S. Barratt, Phil. Trans. Roy. Soc. **A222**, 369 (1922); J. C. McLennan, H. Grayson-Smith and W. T. Collins, Proc. Roy. Soc. **A116**, 277 (1927).

[4] For others, see O. W. Richardson, *Molecular Hydrogen and its Spectrum* (New Haven, 1934).

[5] Some measurements by F. Goos[8] on the change of the intensities in a limited part of the spectrum form a notable exception. They will be discussed later on in this paper.

[6] G. H. Dieke and R. W. Blue, Phys. Rev. **47**, 261 (1935).

[7] The construction of the microphotometer used in this work was aided by a grant from the Rumford Committee of the American Academy of Arts and Sciences, which we acknowledge gratefully. The photometer employs a photronic cell, and it was constructed in such a way that a continuous record of a 15-inch-long plate can be taken.

TABLE I. *Fulcher bands* $2p^3\Pi \rightarrow 2s^3\Sigma$. *Intensities of Q branches.*

K	L	N	H	K	L	N	H	K	H′	He	L	N	H
							0→0					0→1	
1					323	202	60	173.0	110.6	35.6	21.4	10.1	
2					61.5	47.3	25.4	47.0	38.2	174.	4.6	3.0	
3					81.1	81.1	81.1	81.1	81.5	81.1	5.9	5.5	
4					8.7	10.7	24.0	18.5	17.5	19.0	2.4	5.3	
5					8.6	13.2	57.6	21.3	22.9	55.2		1.6	
6							13.5			15.0			
7					1.8	4.9	24.2		6.5	28.8			
8							5.5			8.3			
9						3.2	13.0			19.4			
			1→0				1→1					1→2	
1		14.7	6.1	43.6	391	166	46.9	152.0	86.8	5.9	28.2	24.1	6.2
2		3.5	2.9	10.9	75.4	43.8	23.5	51.0	35.4	4.8	15.8	6.4	3.7
3		15.9	7.0	16.0	77	74.5	96.2	78.7	77.4	15.0	23.2*c*	26.9*c*	21.3*c*
4		1.1	3.3		21.6	8.9	11.9	17.9	16.8	4.7			3.5
5			5.5		1.6	10.7	47.0	19.6	20.4	10.2		1.9	6.9
6			2.4			2.3	12.0			3.6			
7			3.1			3.9	21.0		6.5	7.1		1.7	3.4
8						1.3	4.9			2.9			
9						3.6	9.1			5.0			
			2→1				2→2					2→3	
1		23.2	6.7	60.9	382	154	32.9	137.0	66.0	2.9	199	31.6	7.5
2		8.5	5.0	38.8	68.5	37.5	15.8	44.5	23.6	6.1	31.5	9.4	3.4
3		10.0	9.5	30.0	84.2	59.7	48.1	68.0	48.2	3.9	29.0	15.0	10.5
4		1.7	3.6	4.0	10.1	7.5	14.5	15.8	11.3		4.9	2.6	3.5
5		1.9	6.6	3.8	7.7	10.9	33.3	16.4	14.9	4.5		2.8	7.1
6			2.6			1.4	7.4					.59	2.2
7		1.2	4.0		1.7	2.8	14.6		7.7			.91	3.6
8						.91	3.3						
			3→2				3→3					3→4	
1	57.5*c*	24.1*c*	6.9*c*	73.5*c*	216	101	17.0	91.0	34.7		165	27.4	6.4
2	14.8	6.1	3.2	20.0	39.7	22.4	8.0	32.1	13.4		24.0	8.3	3.4
3	15.5	8.3	6.5	26.3	40.0	31.3	20.2	44.2	21.4		28.9	11.7	7.8
4	6.1*c*	3.8*c*	4.2*c*	17.3*c*	3.1	2.5	5.8				5.7	1.2	
5	2.9	1.3	3.5	2.5	3.1	4.7	17.5	9.6	10.8			1.4	4.4
6													
7						1.1	4.8					.61	2.2
8						.49	1.7					.43	
			4→3				4→4					4→5	
1	22.7	11.0	3.5	26.5	48.5	26.8	6.2	29.6			108	17.1	12.0
2	5.6	3.6	3.5	7.7	9.9	5.0	3.0	12.8			8.5	3.2	2.0
3	6.3*c*	4.6	5.0	13.0	10.6	8.0	9.5	18.0			17.7*c*	7.8	6.4
4	2.7*c*	3.0*c*	*c*	7.1*c*	1.6	1.3	2.8					1.2	2.3
5	1.7*c*	1.1*c*	3.5*c*		1.3	1.2	5.3					1.0	3.2
6						.51	1.9					1.2	2.9
7					1.9*c*	.85	2.4						
			5→4				5→5					5→6	
1	15.4*c*	6.2	3.0		19.2		3.3				29.7	10.0	3.0
2	2.7*c*	1.9			4.7	2.6	1.9				5.9	2.5	2.2
3	3.7	2.9	3.2		5.6	3.9	4.1				7.1	3.8	3.9
4		1.8										.91	2.1
5											*c*	*c*	*c*
			6→5									6→7	
1	7.6	3.9	2.1								14.9	5.7	2.3
2	1.9	1.2										1.8	
3	1.8	1.6	2.7									2.9*c*	

sensitivity of the photographic plates with wavelength. When doubts arose as to the correctness of the calibration, we obtained, through the courtesy of Dr. W. E. Forsythe, another calibrated tungsten lamp which had been calibrated in the G. E. Laboratories by Dr. B. T. Barnes. We compared this lamp with the Eindhoven lamp and found that the results obtained with the two lamps agreed within the limits of experimental errors.

TABLE II. *Intensities of P and R branches.*

K″	L	N	H	K	L	N	H	K	H′	He	L	N	H
							0→0 *P branch*					0→1 *P branch*	
2					39.3	21.6	13.4	24.4	20.3	5.8	9.4	4.2	
3					131.0	90	36.5	67.0	56.3	23.3	7.3	3.7	2.2
4					28.8	24.9	15.8	29.5	20.8	11.4	4.8		
5					31.6	36.0	41.9	36.0	35.9	29.5		1.9	2.2
6					8.5	7.4	18.8	12.9	17.2	10.3			
7					6.7	7.8	26.1	11.7	14.6	23.8		0.74	1.8
8						1.6	6.3			7.2			
9					1.9	3.2	13.0						
							R branch					*R branch*	
0					68.6	37.0	12.1	40.0	25.6	8.4	18.4	4.9	
1					179	130	63	120.0	85.1	28.6	14.3	8.6	
2					30.3*c*	29.3*c*	31.7*c*	34.7*c*	34.2	29.5*c*	5.5*c*	3.5*c*	
3					29.1	29.9	35.1	38.0	29.5	25.5		3.7	
4					6.7	5.2	9.4	10.1	10.3	9.0			
5					3.5	6.2	17.9	10.8	10.2	17.3			
6							5.6			7.6			
7							8.1			10.5			
		1→0 *P branch*					1→1 *P branch*					1→2 *P branch*	
2		2.0		4.9	51.6	22.5	8.0	27.4	14.4	8.1	142*c*	25.8*c*	6.4*c*
3		5.7	3.3	14.1	159	85.6	30.6	69.0	51.1	15.5	45.5	12.3	4.7
4					22.2	14.5	12.2	20.6	17.4	2.3	*c*	*c*	*c*
		R branch					*R branch*					*R branch*	
0		5.0*c*	2.9	13.7*c*	95.2	40	10.3	44.1	23.7	2.8	14.8	5.1	
1		8.3	4.4	27.0	2.1	113	39.4		70.9	6.5	19.8*c*	13.0*c*	
2		1.9	2.2	5.3	31.5	23.4	27.9	32.2	33.6	4.0	5.2	1.6	
3				4.5			12.0			19.3			
		2→1 *P branch*					2→2 *P branch*					2→3 *P branch*	
2		3.4		9.9	49.8	20.4	5.1	26.3	11.9		14.7	8.1*c*	
3		10.5	5.0	32.7	121	65.0	20.6	64.3	33.0		38.5	9.5	3.3
4	4.3	2.6	2.9	7.3	23.1	18.1	25.7	25.2	17.0		11.6	4.1	2.6
5	*c*	*c*	4.1*c*	*c*	27.4	23.0	22.2	32.5	20.5		6.5	3.3	3.7
6		1.6*c*	3.8	2.5*c*								0.84	
					8.7	6.2	14.6	16.2					
		R branch					*R branch*					*R branch*	
0		5.5	2.6	15.7	78.4	33.9	7.5	37.5	17.5		44.0	10.5	3.8
1		11.9	5.9	43.0*c*	87.9	69.1	22.7	69.3	36.4		27.8*c*	23.7	10.1
2			2.5	6.7	23.6	11.6	7.4	21.7	9.5		9.4	4.2	2.6
3		3.3	4.5	9.0	26.1	16.1	17.7	28.0	16.6	2.7	10.1	6.5	6.4
4					5.2	3.5	10.4	11.3	7.2	3.4		1.6	
5									6.4			1.8	
		3→2 *P branch*					3→3 *P branch*					3→4 *P branch*	
2	10.2	3.1		8.6	26.3	6.8	2.5	15.8	6.8		8.9	2.1	
3	28.6	11.3	4.0	30.0	90.5	44.6	11.0	48.5			29.0	8.1	2.8
4	5.1	2.8		7.8	16.9	9.4	5.0	16.1			11.6*c*	49*c*	4.2*c*
		R branch					*R branch*					*R branch*	
0	19.0	5.3	2.6	25.1	39.9	17.1	4.0	21.4	9.5		55.8	8.4	7.6*c*
1	27.8	10.5	4.2	32.7	86.6	41.3	12.3	46.3	17.5		101	23.3	5.7
2	13.0	5.8	3.8	24.9	14.3	7.8	4.3	15.0	7.4		142*c*	25.8*c*	6.4*c*
3						0.56	2.8						

The photographic plates used were the Eastman spectroscopic plates best suited for the various regions. In the infra-red it was necessary to hypersensitize the plates with ammonia. This causes a greater chance for irregularities in that region, which could not be avoided, as without the hypersensitization the plates were too slow. However, the hypersensitization was never pushed to the limit, so that the plates were free from fog. Comparison of different plates in the same region showed that big irregularities did not occur.

The relative intensities derived from the plates were on an arbitrary scale which was different for

TABLE III. *Values of σ and T' for the main Fulcher bands.*

	p IN MM	CURRENT IN MA	0→0		1→1		2→2		3→3		4→4	
			σ	T'	σ	T'	σ	T'	σ	T'	σ	T'
L	0.06	14	0.178	237	0.205	200	0.183	207	0.207	173	0.174	193
N	0.2	400	0.145	290	0.148	271	0.147	258	0.170	210	0.151	222
K	0.17	33	0.119	353	0.119	337	0.120	316	0.127	281		
H′	20	40	0.101	417	0.0972	413	0.0956	397	0.0882	405		
H	20	400	0.0474	888	0.0616	652	0.0467	812	0.0520	687	0.0505	664
He*	0.2 in	400	0.0326	1290	0.0321	1250	0.0307	1240				
He*	150 mm He	400	0.0276	1524								

* The He values are obtained from two different plates taken under slightly different conditions. The lower one is the better plate but contains only the 0→0 band.

each plate. In order to simplify comparison of different plates and also to compare our results with those of Kapuscinski and Eymers, all the results were adjusted to a common scale which was, as much as possible, identical with that of Kapuscinski and Eymers. For this purpose the line $Q(3)$ of the 0→0 Fulcher band ($3p^3\Pi \rightarrow 2s^3\Sigma$) at 6031.900A was taken as the standard line and as its intensity, taken arbitrarily, the value 81.1 of Kapuscinski and Eymers. All intensity values on the different plates were multiplied by a constant factor so that they would agree with this scale. The choice of this intensity standard for plates taken under different conditions is nothing but a convenience and has the result that the average intensity of all the lines is roughly the same.

As the infra-red beyond 7500A could not be compared directly with the standard because one plate covers, at most, a region of 1500A, it was necessary to establish some intermediate standards in the region around 7000A. For this purpose the lines $Q(3)$ of the 0→1 and 1→2 Fulcher bands at 7105.846A and 7179.376A were taken, as their intensity compared to that of the $Q(3)$ lines in the 0→0 and 1→1 bands should be independent of the discharge conditions. These lines were carefully compared with the Fulcher lines around 6000A.

In view of the different adjustments necessary it is obvious that, in general, the relative intensities in a narrow spectral region taken on one plate are more reliable than those over a wide region. As the strong lines were overexposed on a plate which showed the weak lines to best advantage, and vice versa, it was necessary to take in general a weak, a medium, and a strong exposure for each region. In general the figures given do not represent averages of several plates but the actual value of the best plate in the particular region in question, as we found that, especially for the low pressures, the unsteadiness of the discharge is the greatest source of errors. To average two plates taken at slightly different discharge conditions would give less consistent results than to take only one plate, although the mean error is slightly larger. Again, this makes the situation less favorable for the intensities of lines lying in widely different parts of the spectrum than for closely adjacent lines.

3. RESULTS

Our measurements were carried out in the wave-length interval from 5500–8900A. The interval from 5500 to 6400A which is covered both by us and Kapuscinski and Eymers gives ample opportunity to compare the two sets of measurements.

For most of the spectrum, measurements are available only for the three discharges L, N and H mentioned in §2, except for the measurements of Kapuscinski and Eymers for the visible. For the diagonal Fulcher bands we have also the measurements at high pressure and low current density (H′), and those in a mixture of hydrogen and helium (He). Furthermore, there exist for these bands the measurements of Goos[8] for varying pressures and temperatures.

Tables I and II give the intensities measured in the types of discharges mentioned in §2. Furthermore, they include the intensity values of Kapuscinski and Eymers (K) where they are available. A *c* attached to an intensity value means that the line is known to be superimposed

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[8] F. Goos, Zeits. f. Physik **31**, 229 (1924).

TABLE IV. *Comparison between observed and calculated intensities Q branch of 0→0 band*

	L		N		H		H′		K		He	
K	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.	CALC.	OBS.
1	219	323	171.9	202	56.8	60.0	104.7	110.6	200.0	173.0	37.8	38.7
2	59.7	61.5	53.4	47.3	26.1	25.4	38.8	38.2	63.2	47.0	18.8	20.4
3	86.2	81.1	93.8	81.1	82.5	81.1	88.8	81.5	113.8	81.1	66.8	81.1
4	8.9	8.7	12.6	10.7	24.2	24.0	20.0	17.5	15.8	18.5	22.9	22.4
5	8.2	8.6	10.8	13.2	55.2	57.6	22.6	22.9	14.1	21.3	63.8	58.5
6			0.73		12.3		2.7		1.0		18.1	18.0
7							2.2	6.5			42.4	40.0
8											10.3	11.1

by, or confused with, another line and that therefore these values are less reliable. There may be, of course, many unrecognized blends with as yet unclassified lines. Whereas the wavelength measurements of such blends are only slightly affected, the intensities may be completely wrong. A strongly abnormal intensity will in general be an indication that such a blend exists. (See, e.g., the discussion of Table XI). Except for unfavorable lines we can reproduce the measurements to within five percent.

A direct comparison of the measurements of Kapuscinski and Eymers with ours is difficult because they were taken under different conditions. However, by comparing pairs of lines in the red and green which have the same initial state, the relative intensities of which should not be affected by the discharge conditions, we find that the green compared to the red is from two to three times stronger in the K and E measurements than in ours. We assured ourselves that neither our tungsten comparison lamp nor the small remnant astigmatism of our spectrograph could be the cause of the discrepancy. We are at a loss to account for it.

4. THE *Q* BRANCHES
DETERMINATION OF ROTATIONAL TEMPERATURES

If there is thermal equilibrium, the number of molecules in a given rotational state characterized by the rotational quantum number K is proportional to $e^{-E_K/kT}$. These numbers multiplied by a so-called intensity factor involving the *a priori* probability of the state and the transition probability will give the relative intensities in a given band.

For the determination of the temperature from band spectrum intensities, it is assumed that the intensity factors are known and that there is actually thermal equilibrium. We shall see that neither of these conditions is even approximately satisfied in some cases.

The intensity factors are well-known simple functions of K for the standard types of coupling. However, they are affected when interaction with other electronic states occurs, and in many cases more so than the frequencies. Therefore it is advantageous to begin by investigating lines where this interaction is a minimum and this is the case for the Q-branches of the Fulcher bands.[9]

For a Q-branch of a $\Pi\rightarrow\Sigma$ transition the intensities are proportional to $(2K+1)e^{-E_K/kT}$ where, with sufficient approximation,[10] the energy of the initial state is

$$E_K=\text{const.}+\frac{h^2}{8\pi^2\mu r^2}K(K+1)$$
$$=\text{const.}+B_VK(K+1).$$

If we let

$$\sigma=B_V/kT,$$

then the intensities can be written

$$I(K)=A(2K+1)e^{-\sigma K(K+1)},$$

where A is a constant factor independent of K. We must take into account the intensity alternations which, in the H_2 spectrum, cause successive lines in any band to alternate in the ratio 3 : 1. In the following considerations the in-

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[9] G. H. Dieke, Phys. Rev. **48**, 610 (1935).

[10] If there is any need for greater accuracy the actual empirical values for the energy may be used. This would make the computations slightly more bothersome, but not greatly so. However, the increase in accuracy obtained in this way is insignificant compared to the uncertainties due to other causes.

TABLE V. *Effective rotational temperatures computed from Goos' data.*

T	PRESSURE IN MM ACTUAL p	$p_{295°}$	CURRENT IN MA	0→0 σ	0→0 T'	1→1 σ	1→1 T'	2→2 σ	2→2 T'	3→3 σ	3→3 T'
87°	0.06	0.20	4.6	0.231	182	0.227	167	0.286	125		
	0.15	0.51	3.8	0.223	207	0.213	178	0.272	131	0.291	115
	0.69	2.36	3.9	0.188	224	0.159	239	0.241	148	0.281	119
	1.47	4.97	4.0	0.165	255	0.136	279	0.219	163		
295°	0.163	0.163	4.7	0.170	248	0.173	219	0.197	181	0.229	146
	0.326	0.326	3.9	0.162	260	0.163	233	0.198	180	0.213	157
	0.655	0.655	3.6	0.150	280	0.150	253	0.190	188	0.197	170
	1.36	1.36	3.4	0.132	319	0.128	296	0 178	201	0 199	168
495°	0.189	0.114	5.2	0.116	362	0.123	308	0.132	271	0.151	222
	0.41	0.24	3.8	0.102	412	0.109	348	0.129	277	0.141	238
	1.01	0.60	3.8	0.087	485	0.092	412	0.123	290	0.133	252
	2.41	1.47	3.8	0.079	532	0.084	452	0.112	319	0.120	279

tensities of all the weak lines (lines of parahydrogen) are multiplied by 3 to make them directly comparable with the other lines. However, whenever possible, the ortho and para lines have not been mixed in any calculation, although doing so at the high temperatures employed here should not cause any appreciable error.

The temperature may be calculated in the following way:

$$\sigma K(K+1)=\ln A-\ln\frac{I}{2K+1}.$$

By subtracting this for two different values of K the unknown constant A is eliminated. In this way by using the first 5 lines of the various Q branches, the values of σ given in Table III were obtained.

The temperatures T' given in the table are obtained from the relation

$$T'=B/\sigma$$

where $B=h^2/8\pi^2\mu r^2$ is the value for the initial state of the emission. Then with this value of T' or σ the intensities of the lines were calculated, and Table IV shows the agreement between observed and calculated intensities of the 0→0 bands. This is quite satisfactory for the high pressure discharges (H, H′ and He) but far from satisfactory for the normal pressure (N and K). For the low pressure the agreement would be satisfactory if the first line were excluded. The significance of the agreement or the lack of it will be further discussed later.

The calculated temperature is not equal to the room temperature, and the increase above room temperature, which most values show, could easily be explained by saying that the discharge heats the gas and that therefore the temperature inside the discharge tube must be higher. This reasoning, however, does not explain the fact that T' for the low pressure discharge comes out to be 237° in the 0→0 band, more than 50° lower than room temperature. There can be little doubt that this is a real effect, as all the bands show it.

The explanation for the apparent discrepancy lies in the fact that the assumption of thermal equilibrium, necessary to carry out the calculations, is entirely inadequate for these cases. The question of whether or not there is thermal equilibrium in a gas discharge has been considered by many previous investigators, and several instances have been recorded where deviations from the equilibrium distribution were found. The problem has been discussed in detail by Oldenberg.[11] However, practically all these cases are concerned with rather abnormal conditions in the discharge tube, and we have here, perhaps, the first clear case of a decidedly non-equilibrium distribution of a simple diatomic gas in an ordinary discharge. Questions very similar to those treated here were investigated for OH by E. R. Lyman[12] with results partly similar to ours and partly reaching the opposite conclusions. A comparison of these results with ours is not directly possible because of the more complicated mechanism of excitation for the OH

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[11] O. Oldenberg, Phys. Rev. **46**, 210 (1934), where the literature concerning the known cases is given.

[12] E. R. Lyman, Phys. Rev. **53**, 379 (1938).

bands. This is even more true for the results of Rieke[13] on HgH, although there are many points of similarity. Van Wijk[14] investigated this problem for the H_2 discharge with the help of intensity measurements in two violet bands with complicated structure, and came to the conclusion—undoubtedly justified in his case—that there are no serious deviations from the Boltzmann distribution.

As a knowledge of the rotational distribution is quite essential for an understanding of the intensity distribution in all band systems of the H_2 spectrum, we must discuss it somewhat in detail. We see the situation clearly by taking an extreme case where the pressure is so low that the molecule, after it has been excited, has no chance to make a collision before it radiates. The unexcited gas is at equilibrium and the molecules are distributed over the different rotational states as they should be for thermal equilibrium at room temperature. If a discharge is started in this gas the exciting electrons will bring the molecule into an excited state without, however, in first approximation, being able to change the angular momentum of the nuclei. The rotational distribution for the excited molecules is, therefore, still that which corresponds to room temperature equilibrium for the *unexcited* molecule. This is not the room temperature equilibrium for the excited state, which has a much larger moment of inertia. The rotational distribution is determined only by the quantity $\sigma = B/T$. If B changes by a factor $\frac{1}{2}$, the rotational distribution which has remained unchanged looks now like the rotational distribution for the excited molecule at half the room temperature. However, there is no longer equilibrium between rotation and translational motion. The translational temperature $T = 290$ is still room temperature whereas the rotational temperature is $T'_r = 145$. The concept of temperature in the usual sense is, of course, without any meaning.

In the H_2 molecule the B value of the excited $3p^3\Pi$ state is very nearly half that of the normal state, and if there were no collisions we would expect to obtain as the rotational temperature, which is the temperature measured from the rotational distribution in band spectra, just half the value of room temperature.

Actually there are collisions.[15] If nothing but an exchange of rotational and translational energy were concerned, the rotational temperature would be increased and the translational temperature decreased by the collisions until both are equal, or if the collisions with the walls of the vessel are more effective, until the rotational temperature is back to room temperature.

However, in the process of excitation the molecule also has acquired electronic and vibrational energy and the latter especially is capable of being transformed into rotational and translational energy (temperature motion) during a collision.[16] Therefore the temperature of the gas will be increased above room temperature and the increase will be the greater the more collisions take place, i.e., the higher the gas pressure. Of course, there is no justification for speaking of a temperature as long as statistical equilibrium is not fully established. Unless that is the case the distribution over the different rotational states will not be according to Boltzmann's law. The temperatures computed above are only effective rotational temperatures and have the meaning that the actual rotational distribution is closest to the equilibrium (Boltzmann) distribution of that temperature. In the actual discharge tube

TABLE VI. *The intensities of the Fulcher bands. The sum of the intensities of all measured bands is 1510.*

V'	$V''=0$	1	2	3	4	5	6	7
0	355	21						
1	27	326	48					
2		46	261	61				
3			37	137	46			
4				19	35	25		
5					13	17	17	
6						7.8		11

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[13] F. F. Rieke, J. Chem. Phys. **4**, 513 (1936); **5**, 831 (1937). See also W. Kapuscinski and J. G. Eymers, Zeits. f. Physik **54**, 246 (1929).

[14] W. R. van Wijk, Zeits. f. Physik **75**, 584 (1932).

[15] It is not possible to calculate the number of collisions which the excited molecules make, as the collision cross sections are unknown. It must be assumed that they are much larger than the gas kinetic cross section for the normal molecule.

[16] There are, in a discharge, other elementary processes than those discussed in this paper. In a complete analysis of the discharge the relative importance of all these processes would have to be ascertained. It is not our purpose to do this in the present paper. It is evident that a transfer of vibrational energy cannot be the only process causing an increase in temperature, as monatomic gases are also heated by an electrical discharge. It also must be kept in mind that the situation may be entirely different in other molecules, even in different band systems of H_2.

TABLE VII. *Relative intensities of the vibrational transition derived from the Q (1) lines. The intensity of the 0→0 band is taken as 100 in every case.*

	L	K	N	H′	H	He	$T=87°$				$T=295°$				$T=495°$			
$p_{295°}$	0.06	0.2	0.2	20	20	150	0.20	0.51	2.36	5.0	0.16	0.33	0.66	1.36	0.11	0.24	0.60	1.47
0→0	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
1→1	121	88	82	79	78	17	128	111	109	104	108	106	102	100	113	108	103	100
2→2	118	79	76	60	55	8	125	118	114	104	101	100	98	94	105	104	98	92
3→3	67	53	50	31	28		88	77	85	76	71	58	56	57	72	66	60	57
4→4	15	17	13				24	22	32	36	23	23	25	31	23	23	25	26

we have, in addition, the fact that in a pulsating discharge the temperature will change with time and also that the temperature in the middle of the tube will be different from that at the walls, so that the calculated effective temperatures are time and space averages.

Notwithstanding these limitations the effective temperatures are quite useful for a rough description of the state of the gas. Table III shows that the behavior of the actual gas is just what must be expected. At an infinitely low pressure the observed effective temperature should be about 145°K. Collisions have increased this value to 237°K for the lowest observed pressure, and the fact that this value is below room temperature shows that we must be far from equilibrium. The higher the pressure the more excitation energy will be transferred into rotational energy and the higher the temperature. It is noted that Kapuscinski and Eymers had a considerably higher temperature (353°K *vs.* 290°K) at slightly lower pressure and much lower current density than we had. That is easily explained by the fact that their discharge tube was quite different from ours. It had a much narrower capillary and was not water-cooled, so that the temperature would be expected to be higher.

The two high pressure sets H and H′ serve to show the influence of current density. They were taken at identical pressures (20 mm) but H with a current of 0.4A and H′ with a current of 0.04A. This tenfold increase in current density, while nothing else is changed, means approximately a tenfold increase in the number of excited molecules. There is, therefore, a larger transfer of excitation energy into rotational and translational energy with a corresponding increase in temperature.

A comparison of the second and last rows in Table III shows that it makes very little difference whether the collisions of the excited molecules are with other H_2 molecules or with inert atoms like He atoms. The partial pressure of H_2 and the current density are unchanged. The presence of 150 mm of He causes the effective temperature to rise from 290° to 1520°K. This is exactly the opposite of the result obtained by E. R. Lyman[12] for OH. There it was found that the collisions with rare gas atoms were ineffective.

The observations of Goos are entirely in agreement with this. They have been discussed by one of us before[17] and used as proof for the correctness of the classification of the Fulcher bands. However, at that time the knowledge of the structure of molecular spectra was not far enough advanced for quantitative considerations. In Goos' measurements, pressure and temperature are varied independently, which has not been done in any one else's measurements. The pressures given here are the values for the gas at room temperature and are therefore proportional to the density.

Table V, which gives the values of σ and T' calculated from Goos' measurements, shows indeed the variations which we should expect from the preceding arguments. Goos' variations in pressure (from 0.11 to 5 mm) are not as extreme as ours (from 0.06 to 150 mm) and he works with much lower current densities (about 4 ma as compared with 400 ma in most of our experiments). But the changes in the effective temperature are of the same type: For a constant temperature of the tube the effective rotational temperature of the gas increases with increasing gas pressure. Many of the values of T' are below the temperature at which the tube is operated. For a constant density, of course, the effective rotational temperature goes up with the tube

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[17] G. H. Dieke, Zeits. f. Physik **32**, 180 (1925).

temperature. A quantitative comparison with our values is not possible, as the construction of the tubes and the manner in which they were operated is quite different in the two cases.

The much weaker off-diagonal bands in the green and infra-red can be treated in the same way as the diagonal bands, with essentially the same results, but because the bands are so much weaker the results are correspondingly less accurate and are not given in detail.

Table VI gives the intensities of all the measured bands in the Fulcher system. The numbers are approximately the total intensity of all the lines in the bands for discharge type N on the same scale as Table I. The relative intensities of bands in different horizontal rows depends, of course, on the excitation conditions. The values given are obtained from averages with the elimination of the obviously unsuitable lines. The values would be slightly different if the other types of discharges had been used, which must be attributed to the fact that the calibration of the plates for large wave-length intervals is not perfect.

5. The Vibrational Changes

The preceding analysis has established the fact that the chief effect of an increase in pressure in the discharge tube is a marked increase in the effective rotational temperature. At high enough pressures this will be closely equal to the actual gas temperature, as equilibrium will then be nearly reached. A possible mechanism by which the energy necessary for the rise in temperature can be obtained from the discharge becomes apparent by a study of the changes in the vibrational distribution. We leave out of consideration possible effects of the wall of the tube and the complication which arises from the fact that there are several excited electronic states with approximately the same energy, which may be converted into each other by collisions.

Table VII shows the relative intensities of the various $Q(1)$ lines of the main Fulcher sequence. In order to facilitate a comparison, the $Q(1)$ line of the $0\rightarrow 0$ band is arbitrarily taken as 100.

Although the figures show considerable individual variations, their trend is clear. Again the measurements of Goos cannot be directly compared with the others, as Goos' plates were not calibrated for the variation of the sensitivity with wave-length. Only the changes are significant.

The main fact which is revealed by the measurements is that the higher vibrational states become less frequent compared with the zero vibrational state when the pressure is increased. This is one of the effects discussed by Oldenberg.[11]

For infinitely low pressures, when collisions cannot affect the state of affairs, the distribution over the various excited vibrational states is determined by something very similar to the Franck-Condon principle, as the excitation is produced chiefly by electrons which are so light that they cannot affect directly the motion of the nuclei.

In a collision with another molecule (or He atom) the vibrational energy, or part of it, can be transferred into translational or rotational energy of the whole molecule. The excited atom will find itself, after the collision, in a lower vibrational state, possibly also in a different rotational state.

Table VIII shows what percentage of the vibrational states have disappeared compared to the vibrationless state. A number 68, e.g., means that in that particular discharge (N) and vibrational state ($V=1$), 68 percent of the molecules are left at the time radiation occurs, compared to the number which would be left at low pressure and compared to the molecules left in the $V=0$ state. Of course, the actual number of the molecules which disappeared out of that state will be larger, as some will have gone even at the low pressure. The table is derived from the $Q(1)$ lines and in it enter the full experimental errors for these lines. Similar tables can be made for the other Q lines, and these have been taken into account in drawing the conclusions, although the tables themselves have been omitted for brevity's sake.

Table VIII. *Loss of higher vibrational states due to collisions. Percentage of molecules left in the various vibrational states compared to the $V=0$ state and compared to the situation at low pressure.*

V	L	K	N	H′	H	He
0	100	100	100	100	100	100
1	100	73	68	65	65	14
2	100	67	65	51	46	7
3	100	79	75	47	42	
4	100	114	88		69	

Table IX. *The intensity ratios* $P(K+1)/Q(K)$ *and* $R(K-1)/Q(K)$.

	$P(K+1)/Q(K)$							$R(K-1)/Q(K)$						
K	Theor.	L	N	K	H′	H	He	Theor.	L	N	K	H′	H	He
				0 → 0							0 → 0			
1	0.33	0.37	0.32	0.42	0.55	0.67	0.49	0.67	0.64c	0.55c	0.69c	0.69c	0.61c	0.71c
2	0.40	1.72	0.63	0.48	0.59	0.48	0.45	0.60	0.97c	0.92c	0.85c	0.74c	0.83c	0.55c
3	0.43	1.07	0.92	1.09	0.77	0.58	0.42	0.57	1.21	1.08	1.28	1.26	1.17	1.09
4	0.44	1.21	1.22	0.65	0.68	0.58	0.52	0.56	1.11	0.91	0.68	0.56	0.49	0.45
5	0.45	2.96c	1.68c	1.81c	2.25c	0.98c	0.56c	0.55	2.34	1.18	1.42	1.35	0.49	0.49
6						0.64	0.53						0.44	0.38
7						0.78	0.75						0.69	0.79
				1 → 1							1 → 1			
1	0.33	0.40	0.41	0.54	0.50	0.51	4.1	0.67	0.73	0.72	0.87	0.82	0.66	1.42
2	0.40	0.70	0.65	0.45	0.48	0.43	1.08	0.60	0.98	0.86		0.67	0.56	0.45
3	0.43	0.87	0.58	0.79	0.67	0.38	0.46	0.57	1.23c	0.94c	1.23c	1.30c	0.87c	0.80c
				2 → 2							2 → 2			
1	0.33	0.39	0.40	0.82	0.54	0.47		0.67	0.62	0.66	0.82	0.80	0.68	
2	0.40	0.59	0.58	0.48	0.47	0.46		0.60	0.43	0.61	0.52	0.51	0.48	
3	0.43	0.82	0.91	1.11	1.06	1.60		0.57	0.84	0.58	0.96	0.59	0.46	
4	0.44	0.90	1.02	0.69	0.60	0.51		0.56	0.86	0.72	0.59	0.49	0.41	
5								0.55	2.03	0.96	2.07	1.45	0.94	
6						0.66		0.54						
				3 → 3							3 → 3			
1	0.33	0.37	0.20	0.52	0.59	0.44		0.67	0.55	0.51	0.71	0.82	0.71	
2	0.40	0.75	0.66	0.50		0.46		0.60	0.73	0.61	0.48	0.44	0.51	
3	0.43	1.27	0.90	1.09		0.74		0.57	1.07	0.75	1.02	1.04	0.64	

It is quite evident that the higher the pressure, i.e., the larger the number of collisions, the more pronounced is the disappearance of the higher vibrational states. Again the discharge in He with a trace of H_2 forms an extreme case with about 90 percent of the vibrational states removed. The data are not quite clear as to whether the higher vibrational states are more strongly affected than the $V=1$ or $V=2$ states. From the He plates it would appear that the molecules remaining in the $V=2$ state are only about half the number of those in the $V=1$ state, but the discharges with the other conditions do not prove this tendency conclusively. The 4→4 band falls rather out of line, but as this is a very much weaker band than the other bands, it should, perhaps, not count too much.

The comparison of the H and H′ data shows that the vibrational loss is practically independent of the current density. There seems to be a slight but distinctly greater loss for H, which can easily be accounted for by the slightly larger number of collisions due to the higher temperature. This behavior is quite different from the rotational effect, as the temperature increase was considerably larger for the high current density (H). It is, however, just what must be expected. The percentage of molecules disappearing from a given vibrational state is only given by the number of collisions, which are determined essentially by the pressure. For a higher current there will be more excited molecules and more will be taken out by collisions, but the relative number should remain the same. It is different for the rotations. If there are more excited atoms, more vibrational energy can be transferred into temperature motion. As this is distributed over all molecules, excited and unexcited alike, and the total number remains constant, the temperature increase must be larger for a larger current.

In this connection the fact that according to Tables III and VI the higher vibrational states seem to have the lower effective temperatures is of interest. The reality of this effect is by no means certain, but if it is, it would mean that the molecules left in the higher vibrational states have had, in the average, a smaller number of collisions, for there is a definite chance in each collision that the molecule will be removed from that vibrational state. The fewer collisions, the less chance there is for an increase in temperature motion.

The conclusion that in the hydrogen discharge with an excess of helium the higher vibrational states are partly suppressed has already been drawn by Richardson.[4] This matter has been further investigated by Smith,[18] who used pressures of helium as high as 400 mm. He also observed the increase in the intensity of the higher rotational lines and gave an explanation for this substantially the same as that adopted here, namely that vibrational energy is transferred into rotational energy. This was first suggested by Oldenberg[11] in connection with abnormal rotations observed in certain other band spectra.[19]

However, our observations seem to show that in the case of H_2 in an excess of helium, we are not dealing with abnormal rotation, as the effect in helium is only an extreme case of the same effect with moderate or high pressures of pure H_2. Our observations do not agree with Smith's finding that in the $2\rightarrow2$ and $3\rightarrow3$ bands the higher rotational lines are weakened instead of enhanced as in the $0\rightarrow0$ and $1\rightarrow1$ bands. The $3\rightarrow3$ band is too weak for measurement, but on our plates the $2\rightarrow2$ band, although much weaker than the $0\rightarrow0$ and $1\rightarrow1$ bands, shows exactly the same behavior. This is apparent from Tables I and III.

Smith reported that at a pressure of 400 mm of helium the high rotations decrease again. However, Smith's observation at 400 mm was made with a different tube and a current of only 5 ma, whereas all the other observations were made with a current of 35 ma. We have seen that the rotational effect depends decidedly on the current density and should also depend on the type of tube used, so that the observation at 400 mm should not be compared directly with the others.

6. The P and R Branches

It would not be very useful to treat the intensities of the P and R branches in the same way as those of the Q branches were treated in §4. In the first place, the $3p^3\Pi^+$ state which is the initial state of the P and R branches interacts[9] with the $3p^3\Sigma$ state and this interaction gives rise to considerable perturbations in the energy. We must expect that the intensities will also be affected by this interaction so that it is no longer safe to apply the theoretical formulae for the intensity factors.

The observed intensities of the P and R branches seem to be decidedly more irregular than those of the Q branches. These irregularities can be only partly explained by actual irregularities in the transition probabilities. The P and R branches are roughly only half as strong as the Q branches, so that accidental overlappings would affect them more strongly. Further experiments will have to decide the nature of some of these irregularities.

Table IX gives the intensity ratio of the $P(K+1)$ and $R(K-1)$ lines to $Q(K)$. The initial state of all three lines has the same quantum number K and so nearly the same energy that the statistical probability is practically the same. Unless other considerations of a different nature enter, the ratios given in the tables should be simply the ratios of the transition probabilities.

The table shows the surprising fact that contrary to expectations, these ratios are not at all independent of the discharge conditions and that, besides, the values are in most cases entirely different from the theoretical values. Again, indi-

Table X. $P(K+1)/Q(K)$.

$K=$	1	2	3	4	5
$0\rightarrow0$	0.37	1.72	1.07	1.21	2.96 *c*
$1\rightarrow1$	0.40	0.70	0.87		
$2\rightarrow2$	0.39	0.59	0.82	0.90	
$3\rightarrow3$	0.37	0.75	1.27		
Theor.	0.33	0.40	0.43	0.44	0.45

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[18] N. D. Smith, Phys. Rev. **52**, 728 (1937).

[19] There is, however, one fundamental difference between the point of view taken by us and that by Oldenberg and Smith. Oldenberg thinks that the excited H_2 molecule which collides with a helium atom is the one which acquires the high rotational energy while all the others are unaffected, and there is good evidence that this is the case in other band spectra. We believe that before radiation takes place, the vibrational energy is dissipated throughout the whole gas so that a genuine increase in temperature results. To this contribute not only the excited electronic states but also the higher vibrational states of the ground state of the molecule. For most excited molecules after they have emitted one or more quanta of radiation will find themselves back in the ground state of the molecule, but with several quanta of vibrational energy. These will have to be dissipated as temperature motion and, as there will be more molecules of this kind than excited molecules in any of the individual excited states capable of emitting visible radiation, this may be a more important process. In the real gas it is, of course, only a question which picture gives a better approximation, as the true state of affairs is vastly more complex. We believe that the dependence of the rotational effect on the current density and the independence from it of the vibrational effect is good evidence in favor of our point of view. We want, however, to defer a further discussion of this question until the data for other electronic states become available.

TABLE XI. *The intensity ratios $R(K-1)/P(K+1)$.*

K	L	K	N	N′	H	He	Av.	THEOR.
0→0								
1c	1.79	1.64	1.30	1.26	0.63	1.4		2.00
2c	1.37	1.79	1.44	1.51	1.73	1.23		1.50
3	1.05	1.18	1.18	1.64	2.01	2.59		1.33
4	0.92	1.06	0.83	0.82	0.84	0.86	0.85	1.25
5c	0.78	0.78	0.70	0.64	0.50	0.87		1.20
6	0.52	0.92	0.79	0.70	0.69	0.73	0.74	1.17
1→1								
1	1.84	1.61	1.78	1.64	1.29			2.00
2	1.39		1.32	1.38	1.29	0.42	1.35	1.50
3c	1.42	1.56	1.61	1.93	2.29	1.77		1.33
2→2								
1	1.57	1.43	1.66	1.47	1.50		1.55	2.00
2	0.73	1.08	1.06	1.10	1.10		1.08	1.50
3	1.02	0.86	0.64	0.56	0.29			1.33
4	0.95	0.86	0.70	0.81	0.80		0.82	1.25
3→3								
1	1.52	1.35	2.51	1.40	1.60		1.51	2.00
2	0.96	0.95	0.93		1.12		1.00	1.50
3	0.85	0.93	0.83		0.86		0.84	1.33

vidual lines may show widely discordant results due to overlappings, but the general trend stands out quite clearly. Take, for instance, the ratio $P(K+1)/Q(K)$ as function of K for low pressures. These ratios are given in Table X.

For $K=1$ the observed values are very close to the theoretical value and depart from it more and more for increasing K so that at the higher values of K the observed ratios are several times the theoretically expected ones. As this happens at the lowest pressures where the effect of collisions is reduced to a minimum, this increase in the numbers of the Π^+ states with respect to the Π^- states for higher values of K must be due chiefly to the excitation. This is connected with the fact that for the excitation of a $p\Pi^+$ state the assumption made in §4 that the rotational quantum number remains unchanged is not a good approximation. The exact mechanism of the excitation, however, is not yet quite clear, and we leave this point now until the data for other electronic states become available.

If the pressure is increased, the experimental evidence shows that collisions remove the Π^+ states for higher values of K much more effectively than the corresponding Π^- states. This may be due to the fact that the state can interact with other neighboring electronic states, which is not possible for the Π^- state.

Finally the question may be raised whether the transition probabilities themselves do have the values which the simple theory predicts. As the preceding considerations show that we cannot assume that the Boltzmann formula will give us the relative numbers in the various rotational states, we have no way of finding directly the empirical intensity factors which contain the transition probabilities. However, as the lines $R(K-1)$ and $P(K+1)$ issue from the same initial state, the ratio of their intensities should be the ratio of the respective transition probabilities.

Table XI shows that these ratios are indeed independent of the excitation conditions for a number of lines. In the ratios where one of the lines is known to be a blend, the values change considerably and systematically from left to right, either decreasing, as, e.g., $K=1$ in the 0→0 band, or increasing as for $K=3$ of the 1→1 band. There are a few other lines which show the same kind of behavior (e.g., $K=3$ of 0→0 and 2→2 and $K=1$ of 1→1). We must assume that one of the lines involved in these ratios is also a blend. The other ratios show irregular fluctuations of a much smaller magnitude and presumably the lines involved there are free from serious overlappings. The average values are given in these cases (K and He excluded from average). The individual values of these ratios are usually within considerably better than 10 percent of the average, which gives an idea of the accuracy of the measurements.

The important thing is that even in those cases where we have reason to believe that the lines are entirely free from blends, the empirical ratios are quite different from the theoretically expected ones (given in the last column of Table X). Such a discrepancy by as much as 50 percent is likely to be due to the interaction of the $3p^3\Pi$ state with the $3p^3\Sigma$ state, although the magnitude of the discrepancy is surprising for this type of interaction. We shall leave the details of this interaction until we discuss the bands coming from the latter state.

However, the results show how necessary it is to be careful when intensity measurements in band spectra are used to calculate the temperature of the gas or other constants. For in such cases the relative transition probabilities have always been assumed to be the values derived from the elementary theory.