Bands of HD and D$_2$ Ending on the 2$p^1\Sigma$ State

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Two extensive band systems of HD and D$_2$, $3d^1\Sigma\to2p^1\Sigma$ and $3d^1\Pi\to2p^1\Sigma$ are given and described and a few weaker and less complete systems ending on the same state. The rotational constants of $2p^1\Sigma$ can be corrected with the help of the isotopic relations and satisfactory values obtained. There is at present, however, no way to obtain very accurate values of the vibrational constants for any state of the hydrogen molecule. The H$_2$ constants of all the states concerned have been recalculated and from the comparison of the three isotopic molecules much can be learned about the reliability of the constants and other properties of the states. $3d^1\Pi^-$ is strongly decoupled but free from prominent perturbations, whereas $3d^1\Sigma$ and $3d^1\Pi^+$ are strongly perturbed.

PROBABLY the most extensive band system in the spectrum of the hydrogen molecule is that which originates from a transition of the $3d^1\Sigma$ and $3d^1\Pi$ states to the $2p^1\Sigma$ level. These regularities were discovered for H$_2$ by Richardson and Davidson[1] and simultaneously by Mecke and Finkelnburg[2] who gave, however, an interpretation since abandoned. The upper state of the bands, the singlet $3d$ complex, shows several unusual features which make an investigation of the corresponding HD and D$_2$ bands very desirable, and the results of this investigation are given in the present paper.

§1

The manner in which the necessary plate material was obtained has been described before.[3] The bands lie chiefly in the violet and blue region of the spectrum. Most of the wave-length measurements were done in the usual way under the comparator. About 100,000 readings were taken with the measuring machine of Professor Harrison of the Massachusetts Institute of Technology. The readings obtained in this way were afterward corrected so that they show no systematic errors. The relative accuracy of these measurements is only slightly less than those made under the comparator (this refers to our particular kind of plates only) and we were helped considerably by them to obtain a fairly complete list

of wave-lengths in a reasonable time. We wish to express our thanks to Professor Harrison for his cooperation and to Mr. W. Bartlett, who operated the machine.

The intensities given in the tables are again visual estimates only and, as they are obtained from plates taken under very different conditions, they can be relied upon only as rough guides.[4]

The wave numbers and intensities of the bands are listed in Tables I–VI. As in previous cases the analysis of the D$_2$ bands is, in general, more complete than that of the HD bands. The reason for this is that the HD spectrum is best developed in a mixture which contains approximately equal parts H$_2$ and D$_2$. But only 50 percent of this mixture consists of HD molecules, and therefore it is impossible to obtain the HD spectrum without having at the same time the H$_2$ and D$_2$ spectra on the plates. The D$_2$ spectrum, on the other hand, can be obtained pure, and therefore the conditions in this case are much more favorable for observing faint lines.

§2. The 2$p^1\Sigma$ Level

The $2p^1\Sigma$ state, the final level of all the bands under discussion is also the final state of the infrared $2s^1\Sigma\to2p^1\Sigma$ bands described previously.[5] It is the upper level for the so-called "B" bands $2p^1\Sigma\to1s^1\Sigma$ in the far ultraviolet. The analysis of these latter bands has been given by Mie[6] and Fujioka and Wada[7] for HD and by Jeppesen[8]

[1] O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A123**, 54 (1929); **A123**, 466 (1929); **A124**, 50 (1929); **A124**, 69 (1929); **A125**, 23 (1929). O. W. Richardson, *Molecular Hydrogen and its Spectrum* (Yale University Press, 1934), Chapter 5.

[2] W. Finkelnburg and R. Mecke, Zeits. f. Physik **54**, 597 (1929).

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

[4] Quantitative intensity measurements are now being made in this laboratory.

[5] G. H. Dieke, Phys. Rev. **50**, 979 (1936).

[6] K. Mie, Zeits. f. Physik **91**, 475 (1934).

[7] Y. Fujioka and T. Wada, Sc. Papers, Inst. Phys. Chem. Res. **27**, 210 (1935).

[8] C. R. Jeppesen, Phys. Rev. **49**, 797 (1936).

TABLE I. *The $3d^1\Sigma \rightarrow 2p^1\Sigma$ system of HD.*

0→0

J	P BRANCH			R BRANCH		
0	—	—		21502.24	3	
1	21463.02	4		21499.59	5	
2	414.47	3		492.98	4	
3	353.89	4	blend	524.93	4	
4	290.62	1		536.07	5	
5	267.18	1		562.95	5	
6				602.98	6	
7				654.44	3	
8				717.17	2	$+D_2$

0→1

J	P BRANCH			R BRANCH		
0	—	—		20354.88	4	
1	20316.90	2		353.51	6	
2	270.95	0		349.52	5	
3	214.28	3		385.24	8	
4	155.76	1		401.19	8r	
5	138.35	2		434.12	5	
6				481.05	4	
7				540.25	3	
8				610.77	5	blend

0→2

J	P BRANCH			R BRANCH		
0	—	—		19235.68	5	blend
1	19198.98	2		19235.68	5	blend
2	155.14	3		233.75	4	
3	101.74	3		272.72	6v	
4	047.58	2	blend	293.01	6	
5	035.20	00dd		331.01	4	
6				383.98	3	
7				449.88	2	
8				527.19	00	

0→3

J	P BRANCH			R BRANCH		
0	—	—				
1				18144.14	1	blend
2	18065.63	0	$+D_2$	18144.14	1	blend
3				186.13	1	$+D_2$
4				210.16	2	
5				252.81	2	
6				311.27	3	$+H_2$
7				383.28	0	
8				466.55	0	

1→0

J	P BRANCH			R BRANCH		
0	—	—		23383.34	8	blend
1	23342.96	00	$+H_2$	23383.34	8	blend
2	295.61	3		380.47	7	
3	237.63	2		378.28	9b	
4	178.02	1	blend	378.28	9b	blend
5	120.47	0		378.28	9b	blend

1→1

J	P BRANCH			R BRANCH		
0	—	—		22236.13	0	
1	22196.93	0	$+H_2$	237.40	2	blend
2				237.40	2	blend
3				238.81	3	
4				243.22	0	
5				249.66	1	

1→2

J	P BRANCH			R BRANCH		
0	—	—		21117.09	5	
1	21078.81	3	$+H_2$	119.38	6	
2				121.28	6	
3	20985.57	4	$+H_2$	126.11	6	
4	935.06	2		135.14	6	
5	888.61	2	$+H_2$	146.65	5	
6						

1→3

J	P BRANCH			R BRANCH		
0	—	—		20024.63	4	
1				027.87	8	
2	19946.90	3		031.76	9	
3	19898.88	3	blend	039.46	7	
4	852.20	3		052.31	6	
5	810.45	3		068.48	3v	

1→4

J	P BRANCH			R BRANCH		
0	—	—		18957.87	2d	
1				962.35	1	$+D_2$
2				967.66	4	$+D_2$
3	18837.44	1	$+D_2$	978.00	3	
4				994.26	3	
5				19014.70	3	

2→0

J	P BRANCH			R BRANCH		
0	—	—		25266.49	1	
1	25239.32	00		250.49	3	
2				230.72	4	$+H_2$
3				210.95	1	
4				184.36	0	
5				151.51	0	$+H_2$

2→1

J	P BRANCH			R BRANCH		
0	—	—		24118.98	3b	
1	24093.26	00		104.45	4	
2				087.20	3	
3				071.23	3	
4				049.61	4	
5				022.40	0d	

TABLE I.—*Continued.*

2→2

J	P branch			R branch		
0	—	—		23000.08	1	
1				22986.51	3	
2				971.44	2	
3				958.74	2	
4	22785.36	00		941.30	3	
5				919.19	1d	

2→3

J	P branch			R branch		
0	—	—		21907.61	2	+D$_2$
1	21883.80	1		895.04	1	
2				882.06	1ha	
3				871.96	3	
4				858.57	0	
5				841.17	0ha	

2→4

J	P branch			R branch		
0	—	—		20840.77	3	
1	20817.81	4b	blend	829.18	4	
2				817.81	4b	blend
3				810.69	5	+D$_2$
4				800.52	3	
5						

2→5

J	P branch			R branch		
0	—	—		19799.16	3	
1				788.39	5	
2				778.72	5	
3				773.93	3	
4				767.05	5	
5						

3→0

J	P branch			R branch		
0	—	—		27140.34	1	
1	27138.31	0		115.23	3	blend
2				101.21	3	blend
3				101.21	3	blend
4				115.23	3	blend
5				143.71	1	

3→1

J	P branch			R branch		
0	—	—		25993.00	1	
1	25992.23	1	+H$_2$	969.27	1	
2				957.90	2	
3				961.47	1	
4				980.35	1	
5				26014.76	1	

3→2

J	P branch			R branch		
0	—	—		24873.90	0	
1				851.30	1	
2				842.05	1	
3	24717.40	0		848.89	2	+D$_2$
4	656.05	0		872.07	1	
5				911.74	0	

3→3

J	P branch			R branch		
0	—	—		23781.42	00b	
1				760.10	0b	
2				752.51	1	
3				762.26	0	
4	23573.07	00		789.00	0b	
5				833.47	1	

3→4

J	P branch			R branch		
0	—	—				
1	22717.16	0b	+H$_2$	22694.05	00	
2				688.43	0d	
3				700.78	00	
4				730.77	0v	
5				779.72	00	

3→5

J	P branch			R branch		
0	—	—				
1				21653.61	1	

3→6

J	P branch			R branch		
0	—	—				
1				20637.13	7	blend
2				634.77	0	+D$_2$

3→7

J	P branch			R branch		
0	—	—				
1				19645.20	00	+D$_2$
2				644.38	00	+H$_2$

TABLE II. *The 3d¹Σ→2p¹Σ system of D₂.*

0→0

J	P branch		R branch	
0	—	—	21442.05	1
1	21413.48	2	445.95	4
2	382.98	2c	450.64	3
3	347.83	3	459.57	4
4	313.94	1	474.58	4
5	284.96	4	496.66	4
6	262.90	1	526.34	3
7	248.93	2	564.07	4
8	243.50	0d	609.69	3
9	247.72	0	663.24	2
10	261.11	00	724.42	1

0→1

J	P branch		R branch		
0	—	—	20499.68	2	
1	20471.87	2	504.30	5	
2	442.80	1	510.44	4	
3	409.78	3	521.51	6	
4	378.70	1	529.31	5	
5	353.17	1	564.85		*Hβ* ghost
6	335.09	0	598.57	5	
7	325.70	0	640.84	5	
8			691.51	3	
9			750.53	3	
10			817.55	1	

0→2

J	P branch		R branch	
0	—	—	19576.73	1b
1	19549.66	1	582.07	4
2	521.84	0	589.45	2
3	490.65	0	602.36	5
4	462.06	0	622.66	3
5	439.54	0	651.22	5
6	424.97	00	688.47	1
7	419.57	00	734.81	6
8				
9				
10				

0→3

J	P branch		R branch	
0	—	—	18672.20	00
1	18645.56	00	677.99	1
2	618.96	00	686.50	0
3	589.41	00	701.11	2
4	562.89	1	723.61	1
5	543.25	00	754.87	2
6			795.34	0
7			845.28	1

0→4

J	P branch		R branch	
0	—	—		
1			17791.44	00
2				
3			817.14	0
4				
5			875.36	0

1→0

J	P branch		R branch	
0	—	—	22886.24	2
1	22854.31	3	892.93	4
2	827.18	2	896.91	3
3	794.83	3c	901.14	4d
4	760.24	1	915.28	1
5	703.65	00		

1→1

Too weak for observation

1→2

J	P branch			R branch	
0	—	—·		21020.99	1
1	20990.40	2		029.06	4
2	996.03	4	blend	035.74	3
3	937.65	3		043.98	4
4	906.84	1		063.28	0d
5	881.10	2		095.08	3

1→3

J	P branch		R branch	
0	—	—	20116.33	1
1	20086.34	2c	125.03	4
2	063.07	1	132.78	3
3	036.39	2	142.71	4
4			164.19	0d
5	19984.77	1	198.73	2

1→4

J	P branch			R branch	
0	—	—		19229.34	1
1	19199.72	00		238.41	1
2	177.43	1		247.27	0
3	152.45	3	+HD	258.71	1
4				282.35	00

1→5

J	P branch		R branch	
0	—	—	18359.35	0dd
1			368.93	1
2			378.71	1
3			391.59	1

1→6

J	P branch		R branch	
0	—	—		
1			17516.30	1

TABLE III. *The 3d¹Π→2p¹Σ system of HD.*

0→0

J	P branch	int	R branch	int	
0	—	—	21824.15	2	+H₂
1	—	—	913.02	5	
2	21736.36	5			
3	767.46	6			
4	808.14	6			
5	853.68	7			
6	906.35	4			
7	965.41	3			
8	22047.07	0			

0→1

J	P branch	int	R branch	int
0	—	—	20676.82	2
1	—	—	767.11	1
2	20592.87	5		
3	627.77	7		
4	673.33	6		
5	724.83	5		
6	784.40	5		
7	851.17	4		
8	940.84	3		

0→2

J	P branch	int	R branch	int	
0	—	—	19557.80	4	blend
1	—	—	649.17	0	
2	19477.08	1			
3	515.27	3			
4	565.10	4			
5	621.80	2			
6	687.34	2			
7	760.92	1			
8					

0→3

J	P branch	int	R branch	int
0	—	—	18465.28	1
1	—	—	557.73	3
2	18387.62	2		
3	428.81	2		
4	482.27	4		
5	543.59	3		
6	614.47	2		
7	694.29	3		

0→4

J	P branch	int	
0	—	—	
1	—	—	
2			
3	17367.44	00	+D₂
4	424.40	1d	+D₂
5	489.87	3	+H₂

1→0

J	P branch	int	R branch	int
0	—	—	23653.58	4
1	—	—	723.89	2
2	23565.74	4	799.20	3
3	578.27	7	871.37	2
4	596.80	5		
5	613.64	4		

1→1

J	P branch	int	
0	—	—	
1	—	—	
2	22421.64	1bb	+H₂
3	438.71	2	
4	462.11	3	
5	484.77	1	

1→2

J	P branch	int		R branch	int
0	—	—		21387.17	1
1	—	—		459.97	0
2	21306.63	2	+H₂	540.02	0
3	326.07	3		619.17	0
4	353.89	4	blend		
5	381.72	2	+D₂		

1→3

J	P branch	int		R branch	int
0	—	—		20294.70	2
1	—	—		368.44	0
2	20217.00	3	blend		
3	239.62	4b	blend		
4	270.95	0	blend+H₂		
5	303.48	4	+H₂		

1→4

J	P branch	int	R branch	int
0	—	—	19227.97	2
1	—	—	302.62	3
2	19152.95	3		
3	177.99	3		
4	212.99	3		
5	249.79	1		

1→5

J	P branch	int
0	—	—
1	—	—
2	—	—
3	18141.24	0bd

2→0

J	P branch	int		R branch	int	
0	—	—		25387.43	0D	+D₂
1	—	—		448.92	00	
2	25299.73	1				
3	303.37	1				
4	356.80	0				

2→1

J	P branch	int	R branch	int
0	—	—	24240.16	2
1	—	—	303.04	2
2	24156.21	3	415.92	1
3	163.63	3		
4	222.12	2		
5	281.03	00		

TABLE III.—*Continued.*

2→2

J	P BRANCH		R BRANCH	
0	—	—	23121.10	00
1	—	—		
2	23040.47	0		
3	051.09	0		
4	114.06	2	+D₂	
5	178.02	1	blend	

2→3

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	21950.97	1		
3	964.56	1		
4	22031.23	3	+H₂	
5	099.89	0		

2→4

J	P BRANCH		R BRANCH	
0	—	—	20961.95	0
1	—	—	21027.69	0
2	20886.87	3		
3	903.10	3		
4	973.13	4		
5	21046.23	1d		

2→5

J	P BRANCH		R BRANCH	
0	—	—	19920.57	0
1	—	—		
2	19847.55	3D		
3	866.51	2b		
4	939.55	3		
5	20016.55	00	+D₂	

2→6

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	18833.06	0		
3	854.03	0		
4	930.31	00		
5	19011.03	00d		

2→7

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		

3→0

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	—	—		
3	26881.53	00		

3→1

J	P BRANCH		R BRANCH	
0	—	—	25836.49	0
1	—	—	881.11	1
2	25752.45	0		
3	741.84	1		
4	811.78	00		
5	875.97	0		

3→2

J	P BRANCH		R BRANCH		
0	—	—			
1	—	—	24763.18	0	
2	24636.77	1	889.84	00	+H₂
3	629.33	1			
4	703.52	0			
5	772.70	0	+H₂		

3→3

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	23547.24	2		
3	542.72	2		
4	620.70	0		
5	694.55	3	+D₂	

3→4

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	22483.10	2		
3	481.61	1		
4	562.83	1		
5	640.82	2	+D₂	

3→5

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	21444.02	0		
3	444.53	0		
4	529.32	00		
5	611.03	00		

3→6

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	20429.39	2	+D₂	
3	432.23	2		
4	520.00	00		

3→7

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	19439.01	1		
3	444.06	2		
4	534.63	1		
5				

3→8

J	P BRANCH		R BRANCH	
0	—	—		
1	—	—		
2	18472.62	2		
3	479.51	3		
4	573.26	0		

TABLE III.—*Continued.*

J	Q BRANCH			Q BRANCH			Q BRANCH		
	0→0			0→1			0→2		
1	21756.78	5		20610.77	5	blend	19492.82	4	
2	763.03	6		619.54	7	$+H_2$	503.77	5	
3	776.87	6		637.13	7		524.59	5	
4	800.84	5		666.03	6		557.80	4	blend
5	836.55	6		707.71	6		604.67	2	
6	884.80	7d	$+H_2$	763.06	5		665.94	2b	$+H_2$
7	964.68	3		832.45	4		742.21	4	
8	22023.66	0		917.37	1		834.02	00	

J	Q BRANCH			Q BRANCH			Q BRANCH		
	0→3			0→4			1→0		
1	18401.32	4					23595.22	4	blend
2	414.29	5		17350.26	2	$+D_2$	603.23	6	
3	437.97	8b		376.53	00		617.26	7	
4	474.99	7		417.13	0	$+D_2$	639.27	6	
5	526.48	4		472.88	0		670.42	5	$+D_2$
6	593.18	3					711.82	3	
7	675.56	2					766.75	3	$+D_2$
8	773.25	0							

J	Q BRANCH			Q BRANCH			Q BRANCH		
	1→1			1→2			1→3		
1	22449.23	4	$+D_2$	21331.23	3		20239.62	4b	blend
2	459.67	1		344.06	6	$+H_2$	254.40	4	
3	477.60	1		365.10	3		278.46	5	
4	504.38	0		396.24	3		313.38	5	
5	541.69	1		438.59	2		360.37	2	
6	590.09	1	$+D_2$	492.98	4	blend	420.29	2r	
7	652.46	1					495.71	00	

J	Q BRANCH			Q BRANCH			Q BRANCH		
	1→4			1→5			2→0		
1	19173.90	5		18133.29	0		25317.38	2	
2	190.33	6		151.09	2		325.62	3	
3	217.02	4		180.29	1		339.03	3	
4	255.40	3		221.91	1		358.57	3	
5	306.64	3		277.10	1		385.28	1	

J	Q BRANCH			Q BRANCH			Q BRANCH		
	2→1			2→2			2→3		
1	24171.40	4		23053.40	1		21961.98	2	
2	182.14	4		066.39	2		976.90	2	
3	199.28	4		086.78	2		22000.17	4	
4	223.75	3		115.52	1		032.70	2	$+D_2$
5	256.41	3		153.31	0		075.08	0	

J	Q BRANCH			Q BRANCH			Q BRANCH		
	2→4			2→5			2→6		
1	20896.14	4		19855.32	3		18839.07	4	$+D_2$
2	912.80	5		873.72	6	$+H_2$	859.01	4	
3	938.74	5		902.04	3		889.68	3	
4	974.72	4		941.21	3		931.93	4	
5	21021.42	3		991.84	2		986.30	2	

TABLE III.—*Continued.*

J	Q BRANCH			Q BRANCH			Q BRANCH		
	2→7			3→0			3→1		
1	17848.00	4		26915.02	0		25769.04	3	+H₂
2	868.70	0		922.28	0		778.85	2	
3	901.59	0		933.70	0		793.99	2	
4	946.69	0		949.91	0		815.15	3	
5	18004.86	7	+H₂				842.54	2	+D₂
	3→2			3→3			3→4		
1	24651.11	2		23559.59	2				
2	663.06	3		573.55	3				
3	681.50	3		595.22	4	blend	22533.82	00	+D₂
4	706.71	1	+D₂	623.98	3				
5	739.50	1		661.28	3				
	3→5			3→6			3→7		
1	21452.80	1		20436.76	1D		19444.92	2	
2	470.30	2		455.74	3		465.31	3	
3	496.65	3	+D₂	484.35	3		496.25	4	
4	532.49	1		523.13	2		537.82	3b	
5	578.06	1		572.41	2d		590.82	1	
	3→8			4→3			4→4		
1	18477.20	3		25020.50	00				
2	499.04	4		032.56	00				
3	532.06	4		049.93	00				
4	576.51	2		074.91	0				
	4→5			4→6			4→7		
1									
2	22929.30	1		21914.65	00		20924.27	0	
3	951.75	00		939.38	1	+D₂			
4				974.37	1	+D₂			
	4→8								
1									
2	19958.13	00							

TABLE IV. *The 3d¹Π→2p¹Σ system of D₂.*

0→0

J	P branch			R branch	
0	—	—		21710.15	1
1	—	—		769.65	1
2	21651.09	2		839.94	00
3	671.69	5b	blend	917.18	0
4	703.22	2			
5	742.49	3			
6	787.52	2			
7	839.02	3			
8	893.72	1			
9	948.10	1			

0→1

J	P branch			R branch		
0	—	—		20767.97	4	blend
1	—	—		828.07	1	
2	20710.92	1				
3	733.54	5	blend	979.03	00	
4	767.97	4	blend			
5	810.68	5				
6	859.77	4				
7	915.81	5				
8	975.54	2				
9	21035.39	2				

0→2

J	P branch		R branch	
0	—	—		
1	—	—	19905.86	0
2	19789.97	2		
3	814.44	2		
4	851.33	1		
5	897.12	4c		
6	949.64	1		
7	20009.77	2		
8	073.96	0		
9	138.55	0d		

0→3

J	P branch		R branch	
0	—	—		
1	—	—		
2				
3	913.15	0		
4	952.23	0		
5	19000.70	0		
6	056.52	0		
7	120.25	0		

1→0

J	P branch		R branch	
0	—	—	23221.67	2
1	—	—	266.82	2
2	23162.66	2r	319.24	1
3	168.68	3	371.26	1
4	182.55	3		
5	196.70	3		
6	228.37	2		

1→2

J	P branch			R branch	
0	—	—		21356.46	0
1	—	—		402.95	0
2	21301.48	0		457.87	0d
3	311.56	1	blend	514.13	0
4	330.61	1	blend		
5	351.23	2			
6	390.45	1			
7					

1→3

J	P branch		R branch	
0	—	—	20451.82	1
1	—	—	498.85	2
2	20398.49	1	555.13	0
3	410.26	3	612.83	0
4	431.59	2		
5	454.91	2		
6	497.34	1		

1→4

J	P branch			R branch
0	—	—		
1	—	—		
2	19512.95	0		
3	526.28	1		
4	549.66	1	blend	
5	575.42	1		
6	620.83			

1→5

J	P branch		R branch
0	—	—	
1	—	—	
2	18644.41	00	
3	659.14	0	
4	684.38	00	
5	712.53	0	

2→0

J	P branch		R branch	
0	—	—	24665.27	2
1	—	—	706.71	3
2	24606.13	2	752.24	2
3	608.46	4	798.33	3
4	615.60	3		
5	623.71	3		

2→1

J	P branch		R branch	
0	—	—	23723.01	2
1	—	—	764.89	2
2	23666.07	1	812.11	1
3	670.29	3	860.27	2
4	680.34	2		
5	691.92	3		

TABLE IV.—*Continued.*

J	P BRANCH			R BRANCH			J	P BRANCH			R BRANCH		
	2→2							**2→5**					
0	—	—											
1	—	—		22842.70	1								
2	22745.23	1		891.11	0		2	20088.12	0				
3	751.31	1		941.18	0		3	098.92	2				
4	763.74	1					4	117.46	1				
5	778.31	1					5	139.58	3				
	2→3							**2→6**					
0	—	—											
1	—	—											
2							2	19236.25	00				
3	21849.97	0					3	248.41	0				
4	864.61	1					4	268.71	00				
5	881.96	0					5	293.02	1				
	2→4							**2→7**					
0	—	—											
1	—	—											
2	20956.64	0					2						
3	966.03	4	blend				3	18414.31	0				
4	982.71	1					4	436.32	0				
5	21002.49	0					5	462.75	1				

J	Q BRANCH			Q BRANCH			Q BRANCH		
	0→0			**0→1**			**0→2**		
1	21671.69	6	blend	20730.10	5		19807.88	3	
2	681.05	3		740.86	4		819.89	1	
3	695.92	4		757.88	5		838.76	4	
4	717.17	3		781.93	4		865.29	1	
5	745.60	3		813.72	6		900.09	3	
6	781.56	2		853.81	5		943.69	1	
7	825.72	3		902.47	5		996.43	1	
	0→3			**0→4**					
1	18903.79	1		18017.26	00				
2	916.92	0							
3	937.48	2		053.46	00				
4	966.24	0							
5	19003.75	1							
6	050.54	0							
7	106.93	0							
	1→0			**1→1**			**1→2**		
1	23192.22	4		Too weak for observation			21328.33	2	
2	201.26	3					340.13	2	
3	215.46	4					358.29	3	
4	235.19	3					383.28	2c	
5	261.04	4					415.56	2	
6	293.36	2					455.47	1	
7	332.58	2					503.29	1	

TABLE IV.—*Continued.*

J	Q BRANCH 1→3			Q BRANCH 1→4			Q BRANCH 1→5	
1	20424.29	4		19537.73	3		18668.21	1
2	437.20	2		551.67	1		683.14	1
3	457.04	4		573.03	4		705.91	2
4	484.23	4		602.36	5	blend	737.04	0
5	519.19	4		639.75	2			
6	562.34	1		685.80	0			
7	613.60	5b	blend	740.63	1			

J	Q BRANCH 2→0			Q BRANCH 2→1			Q BRANCH 2→2	
1	24636.15	4		23694.54	3		22772.33	2
2	644.65	3		704.44	2		783.50	1
3	657.47	5		719.57	3		800.50	2
4	675.47	4		740.25	3		823.55	1d
5	698.53	4		766.75	3		853.14	2
6	727.10	3		799.35	2		889.27	0v
7	761.60	4		838.35	2		932.28	1
8	802.09	1		884.00	1			
9				936.24	1			

J	Q BRANCH 2→3			Q BRANCH 2→4			Q BRANCH 2→5	
1	21868.14	0		20981.69	3		20112.18	3
2	880.48	00		995.00	2		126.46	1
3	899.15	0		015.23	5		148.12	4
4				042.60	2		177.36	2
5	956.69	00		077.33	3		214.42	3
6				119.63	2b		259.53	2
7				169.66	1			
8				227.57	0			

J	Q BRANCH 2→6			Q BRANCH 2→7		
1	19259.44	2		18423.22	1	
2	274.61	1		439.30	0	
3	297.61	3		463.51	2	
4	328.65	1		496.25	0	
5	367.90	2		537.57	0	
6	415.57	0		587.80	00	
7	471.75	0		646.76	1	

J	Q BRANCH 3→0			Q BRANCH 3→1			Q BRANCH 3→2	
1	26000.46	00		25058.84	2		24136.59	4
2	008.03	2		067.80	4		146.81	4
3	019.41	3		081.41	6		162.26	5
4	035.08	2		099.86	6		183.21	3
5	055.09	2		123.31	6		209.66	4
6	079.66	0		152.06	4		241.91	00
7	109.29	0		186.16	4			
8				225.96	1			
9				271.28	00			

TABLE IV.—*Continued*.

J	Q BRANCH			Q BRANCH			Q BRANCH		
	3→3			3→4			3→5		
1	23232.54	2		22345.99	00dc		21476.45	0	
2	243.86	2		358.10	0v		489.67	0db	
3	261.04	4	blend	377.09	00		509.93	1	
4	284.23	2b		402.14	0		536.99	1	
5	313.34	2		433.90	0		571.01	1	
6	348.78	1		472.31	1				
7	390.61	1							
8									
9									
	3→6			3→7			3→8		
1	20623.72	2		19787.54	2		18967.66	1	
2	637.96	1		802.63	1		983.55	1	
3	659.42	4		825.36	3		19007.52	2	
4	688.21	1		855.81	1		039.58	1	
5	724.42	2		894.14	2		079.88	2	
6	767.97	4	blend	940.38	0				
7	819.53	1		994.58	0d				
	3→9								
1	18163.97	0							
2	180.66	0							
3	205.79	1							
	4→1			4→2			4→3		
1	26336.94	3		25414.68	5		24510.68	00	
2	344.79	2		423.84	5D				
3	356.46	3		437.34	6		536.17	1	
4	372.38	1		455.66	4		556.56	00	
5	392.35	2		478.78	5		582.52	0	
6	417.03	0		506.98	3				
7	446.30	0		540.22	3				
	4→4			4→5			4→6		
1	23624.03	3		22754.59	0		Too weak for observation.		
2	635.22	2		766.67	1				
3	652.03	3		784.96	1				
4	674.59	1		809.43	2				
5	702.95	2		840.08	1				
6	737.24	0							
7	777.56	1							
	4→7			4→8			4→9		
1	21065.65	1		20245.79	1		19442.11	1d	
2	079.52	1d		260.48	1		457.61	0	
3	100.40	2		282.52	3		480.85	1	
4	128.30	0		312.08	0		511.82	0d	
5	163.25	1		349.01	1		550.74	0	
6	205.32	00		393.47	00				
7	254.57	00		445.37	0				

TABLE V.

The $3d^1\Delta \rightarrow 2p^1\Sigma$ system of HD.

J	P BRANCH			R BRANCH		
	0→0					
1	—	—		22128.78	00	
2	—	—		267.85	00	
3	21983.20	0				
4	22065.47	00				
	0→1					
1	—	—		20982.69	2	
2	—	—		21124.55	1	
3	20843.26	1d				
4	930.68	00	blend			
	0→2					
1	—	—				
2						
3						
4	19822.64	00				
	0→3					
1	—	—				
2						
3	18644.41	0	+D₂			
4	739.71	1				

J	P BRANCH			R BRANCH		
	1→0					
1	—	—				
2	—	—				
3						
4	23896.46	00				
	1→1					
1	—	—				
2	—	—				
3						
4	22761.76	1	+H₂ / +D₂			
	1→2					
1	—	—				
2	—	—				
3						
4	21653.61	1	blend			
	1→3					
1	—	—				
2	—	—				
3						
4	20570.51	0				
	1→4					

J	Q BRANCH			Q BRANCH			Q BRANCH		
	0→0			**0→1**			**0→2**		
0	—	—		—	—		—	—	
1	—	—							
2	22074.23	0	+D²	20930.68	00	blend			
3	151.28	2		21011.68	0				
4	200.74	1		066.10	00		19958.13	00	blend
	0→3			**1→0**			**1→1**		
1	—	—		—	—		—	—	
2	18725.47	0		23907.06	00		22763.64	2	+D₂
3	812.59	0		982.17	0d		842.50	2	
4	875.25	00		24023.22	0		888.68	0	
	1→2			**1→3**			**1→4**		
0	—	—		—	—				
1	—	—		—	—				
2	21647.76	0		20558.34	0				
3	729.91	0							
4	780.23	0							

TABLE V.—*Continued.*

The $3^1K \rightarrow 2p^1\Sigma$ system of HD.

J	P BRANCH			R BRANCH		
			0→0			
0	—	—		21363.21	1	blend
1				21363.21	1	blend
2						
3				21339.56	1	
			0→1			
0	—	—		20215.90	1b	blend
1				217.00	3	blend
2	20132.18	0		215.90	1b	blend
3				199.90	2	
			0→2			
0	—	—		19096.55	2	
1				099.01	2	
2				19100.03	3b	
3	18965.11	00		087.39	2	
			1→0			
0	—	—				
1				23344.28	3	
2						
3				23304.97	0	
			1→1			
0	—	—				
1						
2				22198.34	00b	
3				22165.23	3	+D₂
4				090.16	00	
			1→2			
0	—	—		21076.12	2	+H₂
1				080.30	3	
2				081.78	3	+H₂
3				052.58	3	
4				20981.70	3	+D₂

J	P BRANCH			R BRANCH		
			1→3			
0	—	—		19983.60	0	
1				988.80	3	
2				992.44	2	
3				965.95	3	
4				898.88	3	blend

The $3^1M \rightarrow 2p^1\Sigma$ system of HD.

J	P BRANCH			R BRANCH		
			α→0			
0						
1	22753.13	1		22815.64	2	
2				22798.89	3	
3	22670.06	1	+D₂	809.39	2	+D₂
4	596.26	0				
			α→1			
0						
1	21607.14	0		21669.66	0	blend
2				21655.41	0	
3	530.33	0	+D₂	669.66	0	blend
			α→2			
0						
1	20489.42	0	+D₂	20551.79	0	
2				20539.33	3	+D₂
3	418.08	00		557.06	00	
			α→3			
0	—	—				
1						
2				19449.88	2	blend
3				470.47	00	

TABLE VI.

The $3^1K\rightarrow2p^1\Sigma$ system of D_2.

J	P BRANCH			R BRANCH		
			0→0			
0	—					
1				21279.94	1	
2	21199.71	00		21265.61	0	
3				21250.55	2	
4						
			0→1			
0	—					
1				20338.15	0	
2	20259.53	1b		20325.70	0	+HD
3				20312.70	1	
			0→2			
0	—					
1				19416.04	00	
2	19338.61	00				
3				19393.61	00	
			1→0			
0	—					
1				22943.14	00	
			1→1			
0	—					
1				22001.62	00	blend
2				22001.62	00	blend
3	21900.50	0		21988.24	00	
4						
5	21820.31	00				
			1→2			
0	—					
1				21079.52	1d	blend
2				21080.51	00	
3	20981.70	3	+HD	21069.43	0	
4				21040.27	00	
5	20894.50	2	+HD			

J	P BRANCH			R BRANCH		
			1→3			
0	—	—				
1						
2						
3				20168.27	00	
4				20141.04	00	

$3^1M\rightarrow2p^1\Sigma$ system of D_2.

J	P BRANCH			R BRANCH		
			a→0			
0	—	—		22339.38	0	
1	22304.49	1		328.24*	1	
2	280.48	0	+HD	317.12	0	
3	230.24	1		298.77	2	
4	180.40	0				
5	124.25	1				
			a→1			
0	—	—		21396.97	0	
1	21362.99	0		386.46	00	
2	340.13	2	blend			
3	292.25	0		360.53	00	
			a→2			
0	—	—				
1						
2	20420.29	00dd	+HD			
3						
4	20328.76	00				
			a→3			
0	—	—				
1	19536.34	00d				
2						
3	19471.75	0				
4	429.58	0				
			a→4			
3	18587.80	00				

for D_2. We shall see that the results of our analysis agree well with the data obtained from the far ultraviolet bands, except that our results must be expected to have about a 50-fold accuracy.

Table VII gives the averages of the rotational differences obtained directly from the differences $R(J-1)-P(J+1)$ except those marked with an asterisk which are obtained in a more indirect way. It is a characteristic of the bands in question

that usually, if the R branch is well developed, the P branch is extremely weak and partly absent in the less intensive bands, and *vice versa*. This means that especially for the higher vibrational levels the $R(J-1)-P(J+1)$ differences cannot be obtained. They can, however, be calculated if those of some other vibrational level are known with the help of the vibrational differences for any branch, e.g. the Q branches. For

instance, if we know the rotational differences $F_0(J+1)-F_0(J-1)$ of the $V=0$ state, we can find the corresponding differences for the $V=1$ state in the following way.

$$F_1(J+1)-F_1(J-1) = F_0(J+1)-F_0(J-1)$$
$$+Q_{a\to0}(J+1)-Q_{a\to1}(J+1)$$
$$-Q_{a\to0}(J-1)+Q_{a\to1}(J-1),$$

in which a is any value of the initial vibrational quantum number. Atlhough there are now more lines involved in the calculation of a single difference which would increase the magnitude of the probable error, this is counteracted by the fact that the vibrational differences $Q_{a\to0}(J)$ $-Q_{a\to1}(J)$ etc., can be obtained as averages of many independent values from strong lines. The rotational HD differences for $J\geq5$ and $V=0$ were extrapolated with formula (1), as they could not be determined directly for any value of V.

If the rotational energy is represented by the usual formula

$$E_V(J) = B_V J(J+1) - D_V J^2(J+1)^2 + \cdots \quad (1)$$

the constants B_V and D_V can be calculated in the customary way from the differences of Table VII. They are collected in Table VIII which contains also the corresponding constants for H_2 which were recalculated from Richardson and Davidson's data[1] and the vibrational differences

$\omega_{n+1,\ n}$. We give two sets of these differences. The first set contains the differences between successive vibrational levels with $J=0$. This is the usually adopted procedure. There is, however for a $p\Sigma$ state, a term $2B_V$ which should properly be counted as belonging also to the rotational energy. If this term is first subtracted and then the vibrational differences taken, we obtain the second set which contains the correction Δ_b discussed in the next paragraph.

The lower part of Table VIII contains the constants occurring in the expression[9]

$$B_V = \sum_l Y_{l1}(V+\tfrac{1}{2})^l \quad (2)$$

and the formula for the vibrational energy

$$W_V = \sum_n Y_{n0}(V+\tfrac{1}{2})^n. \quad (3)$$

---

[9] In what follows the more systematic expressions Y_{lm} occurring in the formula

$$W = \sum_{l,\ m} Y_{lm}(V+\tfrac{1}{2})^l J^m (J+1)^m$$

for the vibration-rotation energy are used rather than the conventional symbols B_e, ω, x etc. In Table VIII, both designations are given for comparison. We make, however, a distinction between Y_{01} and B_e. Y_{01} is the constant obtained by extrapolating according to (2) the empirical B_V values to $V=0$ whereas $B_e = h/8\pi^2 c\mu r_e^2$ in which r_e is the equilibrium distance for the molecule with nonrotating and nonvibrating nuclei. B_e can be obtained from Y_{01} by applying the corrections discussed in the next paragraph. A similar distinction is observed for Y_{10} and ω_e.

TABLE VII. *Rotational differences* $F(J+1)-F(J-1)$ *for* $2p^1\Sigma$.

J	$V=0$	1	2	3	4	5	6	7	8	9
				HD						
1	87.80	83.97	80.63	77.70	75.05	72.80*	70.37*	68.11*	66.23*	
2	145.62	139.31	133.88	128.90	124.61	120.73*	116.81*	112.99*	109.82*	
3	202.38	193.78	186.11	179.50	173.29*	167.64*	162.38*	157.29*	152.33*	
4	257.74	246.91*	237.45*	229.09*	221.33*	214.22*	207.43*	200.90*		
5	311.19*	298.33*	287.22*	277.21*						
6	362.35*	347.69*	334.95*	323.35*						
7	410.81*	395.13*	381.40*	369.36*						
				D₂						
1	59.06	56.90	54.93	53.29	51.81*	50.37*	49.04*	47.75*	46.53*	45.37*
2	98.13	94.53	91.41	88.59	86.11*	83.73*	81.51*	79.40*	75.39*	75.41*
3	136.67	131.75	127.40	123.53	119.88*	116.55*	113.45*	110.53*	107.69*	105.07*
4	174.62	168.35	162.86	157.93	153.43*	149.21*	145.26*	141.46*	137.85*	134.42*
5	211.68	204.22	197.69	191.70*	186.33*	181.22*	176.43*	171.80	167.43*	
6	247.73	239.16*	231.65	224.78*						
7	282.84	273.22*	264.70*							
8	316.35	305.83*	296.62*							
9	348.58	337.31*								

Table VIII. *Constants of the $2p^1\Sigma$-level.*

	H₂		HD	D₂	
B_0	19.434	19.457*	14.685	9.866	9.827*
B_1	18.460	18.482	14.041	9.503	9.495
B_2	17.641	17.652	13.482	9.187	9.196
B_3	16.913	16.933	12.982	8.903	8.898
B_4	16.246	16.265	12.544	8.642	8.582
B_5	15.637	15.626	12.146	8.400	8.390
B_6	15.055	15.004	11.75	8.177	8.178
B_7	14.477	14.410	11.37	7.966	7.966
B_8			11.10	7.762	
B_9				7.571	
D_0	0.0147		0.00874	0.00395	
D_1	126		779	357	
D_2	114		714	323	
D_3	102		623	304	
D_4	093		613	280	
D_5	086		603	261	
D_6	078		557	253	
D_7	069		529	252	
D_8				241	
D_9				244	

Vibrational differences

	For $J=0$	corrected	for $J=0$	corrected	for $J=0$	corrected
ω_{10}	1318.349	1320.299	1147.30	1148.59	942.344	943.071
ω_{21}	1281.472	1283.109	1119.105	1120.223	922.861	923.473
ω_{32}	1246.71	1248.146	1092.46	1093.46	904.631	905.198
ω_{43}	1213.04	1214.373	1066.65	1067.52	887.061	887.583
ω_{54}	1179.97	1181.191	1042.30	1042.30	869.986	870.470
ω_{65}	1147.47	1148.63	1016.99	1017.78	853.179	853.625
ω_{76}	1115.47	1116.626	992.66	993.42	836.608	837.029
ω_{87}			968.214	968.75	820.283	820.692
ω_{98}					804.041	804.423

		H₂	HD	D₂
α	Y_{01}	20.0109	15.0549	10.0716
	$-\,Y_{11}$	1.227	0.781	0.429
β	Y_{21}	0.160	0.0890	0.0391
γ	$-\,Y_{31}$	0.0231	0.0145	0.00408
δ	Y_{41}	0.0015	0.0013	0.00020
D_e	Y_{02}	0.0156	0.00949	0.00410
	$-\,Y_{12}$	0.0020	0.0013	0.00040
	Y_{22}	0.00014	0.00012	0.000024
x	Y_{10}	1360.634	1179.218	964.403
y	$-\,Y_{20}$	21.253	16.091	11.269
z	Y_{30}	0.738	0.528	0.410
	$-\,Y_{40}$	0.045	0.032	0.025
	B_e	20.2758	15.2050	10.1387
	$\overline{B}_e$	20.2485	15.1896	10.1319
	$I\cdot 10^{40}$	1.3659	1.8211	2.7298
	$r_e\cdot 10^8$	1.2819	1.2821	1.2819
	ω_e	1363.03	1180.77	965.249

* From the ultraviolet $2p^1\Sigma \rightarrow 1s^1\Sigma$ bands.

TABLE IX. *Comparison of the constants of $2p^1\Sigma$ for (1) H_2, (2) HD and (3) D_2.*

		HD : H_2	D_2 : H_2	D_2 : HD	n
		Theoretical values			
ρ		0.86613	0.70737	0.81670	1
ρ^2		0.75019	0.50038	0.66700	2
ρ^3		0.6498	0.3540	0.5447	3
ρ^4		0.5628	0.2504	0.4449	4
ρ^5		0.4874	0.1771	0.3633	5
		Observed ratios			
	Y_{01}	0.75233	0.50331	0.66899	3
α	$-Y_{11}$	0.6365	0.3498	0.5500	2
β	Y_{21}	0.557	0.245	0.439	4
γ	$-Y_{31}$	0.628	0.177	0.281	5
δ	Y_{41}	0.867	0.133	0.154	6
D_e	Y_{02}	0.6083	0.2628	0.4320	4
	$-Y_{12}$	0.650	0.200	0.308	5
	Y_{22}	0.857	0.171	0.200	6
	Y_{10}	0.86667	0.70879	0.81783	1
x	$-Y_{20}$	0.75712	0.53023	0.70633	2
y	Y_{30}	0.71545	0.55556	0.77652	3
z	$-Y_{40}$	0.711	0.556	0.781	4
B_e		0.74991	0.50004	0.66680	2
$\overline{B}_e$		0.75016	0.50038	0.66703	2
ω_e		0.86629	0.70816	0.81747	1

In Table VIII are also listed (in small print) the B_V values of H_2 [10] and D_2 [8] obtained from the far ultraviolet bands for which $2p^1\Sigma$ is the upper level. (Those for HD are not given by the authors.) A comparison of these with our values shows that the agreement is as good as can be expected.

§3. COMPARISON OF THE CONSTANTS OF THE $2p^1\Sigma$ STATE FOR H_2, HD AND D_2

The formulae used for the calculation of the constants are only approximations and the reliability of the values obtained for these constants depends on how well these approximations represent the actual data. By comparing corresponding constants for the three molecules H_2, HD and D_2 we can get an idea of their reliability. In Table IX the ratios of the constants are given. These ratios should be equal, according to the elementary theory, to powers of the isotopic mass factor $\rho_{ij} = (\mu_i/\mu_j)^{\frac{1}{2}}$. The exponent n and the theoretical values of $\rho_{ij}{}^n$ calculated from the known masses of the H and D atoms are also given

[10] C. R. Jeppesen, Phys. Rev. 44, 165 (1933).

in the table.[11] From the table it appears that the agreement between the observed ratios of the constants and their theoretical values is not very good, in most cases much less than would be warranted by the errors of the measurements. The reasons for this discrepancy lie in the nature of the $2p^1\Sigma$ state.

The elementary relations between the vibrational and rotational constants of isotopic molecules hold only if the various interactions between electronic motion and rotation and vibration can be neglected and not even then, as Dunham has shown that even for the ordinary rotating oscillator there are small corrections which will change the isotopic ratios.

The various corrections which have to be applied to obtain the constants of the nonrotating, nonvibrating molecule free from interactions have been given by various investigators.[12] More recently, Van Vleck[13] has discussed systematically

[11] Jordan and Bainbridge, Phys. Rev. 51, 385 (1937).
[12] Dunham, Phys. Rev. 41, 721 (1932); R. de L. Kronig, Physica 1, 617 (1934); G. H. Dieke, Phys. Rev. 47, 661 (1935).
[13] J. H. Van Vleck, J. Chem. Phys. 4, 327 (1936).

all these corrections and their interrelations and limitations. The constants, after the corrections have been applied, should satisfy the elementary isotope relations.

Let us consider Y_{01} first and designate by B_e the corrected value. If we call the various corrections Γ_a, Γ_b etc. we have[12, 13]

$$Y_{01}=B_e+\Gamma_a+\Gamma_b+\Gamma_c=B_e+\Gamma$$

with

$$\Gamma_a=\frac{B_e^3}{2\omega_e^2}[15-23a_1a_2+14a_1-9a_2+15a_3$$
$$+10.5(a_1^2+a_1^3)],$$

$$\Gamma_b=\frac{-16B_e^3}{\omega_e^2},$$

$$\Gamma_c=\frac{-4B_e^2}{\delta}. \tag{4}$$

Γ_c is due to the interaction with the $2p^1\Pi$ state which lies about $\delta=8890$ cm^{-1} above the $2p^1\Sigma$ state.

Γ_a requires the knowledge of the constants which occur in the expression

$$V=ha_0\xi^2(1+a_1\xi+a_2^!\xi^2+\cdots)$$

for the potential energy. They can be obtained from the approximate relations

$$Y_{11}=\frac{6B_e^2}{\omega_e}(1+a_1),$$

$$Y_{20}=1.5B_e(a_2-5/4a_1^2),$$

$$Y_{21}=\frac{6B_e^3}{\omega_e^2}[5+10a_1-3a_2+5a_3-13a_1a_2$$
$$+7.5(a_1^2+a_1^3)], \tag{5}$$

$$Y_{30}=\frac{B_e^2}{2\omega_e}[10a_4-35a_1a_3-8.5a_2^2$$
$$+225a_1^2a_2/4-705a_1^4/32],$$

and are found to be

$$a_1=-1.680,$$
$$a_2=2.781,$$
$$a_3=-4.055,$$
$$a_4=4.59.$$

They are calculated from the constants of D_2 as the relations (5) hold best for that molecule.

a_3 and especially a_4 are not very reliable as they come out as differences between rather big numbers which all have a considerable possible error.

The values of these constants can now be substituted into (4) and the corrections calculated. They turn out to be all negative and have the values

	H$_2$	HD	D$_2$
$-\Gamma_a$	0.0155	0.0087	0.0039
$-\Gamma_b$	0.0692	0.0394	0.0176
$-\Gamma_c$	0.1802	0.1020	0.0456
$-\Gamma$	0.2649	0.1501	0.0671

If the total correction Γ is applied to Y_{01} we get the values B_e given in Table VIII, and the isotopic ratios in Table IX. We note that the discrepancy between the observed and theoretical ratios is much smaller but still too big to be accounted for entirely by experimental errors.

There are several possible explanations for this remaining discrepancy. In the first place the corrections (4) are derived under certain simplifying assumptions. E.g. Γ_c is derived under the assumption that the orbital angular momentum $L=1$ is constant in magnitude and precesses about the internuclear axis, and further that the $2p^1\Pi$ state is the only state by which $2p^1\Sigma$ is affected. That is certainly not rigorously the case, but a calculation of the exact nature of the other influences would presuppose a knowledge of the structure of the wave functions of the states which we do not yet possess. But in first approximation these additional corrections should have the same isotopic factor ρ^4 as those given in (4). If we grant this, it is possible to find the magnitude of the correction and therefore the true value of B_e and the internuclear distance by a comparison of the three isotopic molecules in the following manner. Let us call $\bar{B}_e$ the true value of B_e while B_e is the observed value (with the corrections (4) applied) and q as yet the unknown magnitude of the correction for H$_2$ so that

$$B_e=\bar{B}_e+q.$$

Then for the two other molecules the value of B_e becomes $\rho^2\bar{B}_e+\rho^4q$ so that the observed ratio ρ'^2 is

$$\frac{\rho^2\bar{B}_e+\rho^4q}{\bar{B}_e+q}=\rho^2\frac{B_e-(1-\rho^2)q}{Be}=\rho'^2,$$

from which follows

$$q = -\frac{B_e}{1-\rho^2}\left(\frac{\rho'^2}{\rho^2}-1\right). \qquad (6)$$

In this expression $\rho = \rho_{12}$, if we compare H_2 with HD and we obtain $q = -0.0300$. If we compare H_2 with D_2 ($\rho = \rho_{13}$) we find $q = -0.0276$. The good agreement of these two entirely independent values is a good argument in favor of our assumption. We can now find the values of $\bar{B}_e$ by adding to B_e q for H_2, $\rho_{12}{}^4q$ for HD, and $\rho_{13}{}^4q$ for D_2. Those values are also given in Table VIII. They are believed to be as near to the true values of B_e as it is possible to get at present. The values of the moment of inertia I and the equilibrium distance r_e derived from them are listed as well. Table IX shows that the agreement of the $\bar{B}_e$ ratios with the theoretical values is now within the limits of experimental errors. The influence of the mass of an electron on the moments of inertia would now be considerably bigger than the discrepancy between the theoretical values of ρ^2 and the observed ratios of $\bar{B}_e$.

There is, however, another source of errors which is only partly compensated for by the above calculations. We recognize it best if we realize how the values of B_e are originally obtained, by fitting the formula (2) to the values of B_V and then extrapolate to $V=0$. This formula converges well only for small values of V and by neglecting the higher terms we may get an appreciable error in all the constants. It is difficult to estimate the magnitude of this error, but very likely it is not very prominent for B_e, as the convergence of the series is relatively good for the values of V used for the calculation of the constants.

The other rotational constants Y_{11}, Y_{21}, Y_{02}, Y_{12}, etc. are affected by the interactions discussed above in a way similar to Y_{01} but less easily amenable to an exact numerical evaluation. We shall omit, therefore, a discussion of these corrections now, but hope to return to them in a subsequent paper when we shall discuss the structure of the $2p^1\Pi$ state. It is obvious though from Table IX that the values of Y_{31} and Y_{41} can have no significance at all, which is not surprising, as they are very strongly influenced by small errors in the measurements.

Before we are able to judge the agreement between the theoretical values of ρ_{ij} and the ratios of the values of ω_e, we must apply corrections similar to those given in (4) for B_e. If we call these corrections Δ_a, Δ_b etc. we have

$$\Delta_a = \frac{B_e{}^2}{32\omega_e}(200a_4 - 380a_1a_3 - 134a_2{}^2$$
$$+459a_1{}^2a_2 - 1155a_1{}^4/8), \qquad (7)$$
$$\Delta_b = -2Y_{11}.$$

There is a third correction Δ_d due to the interaction of $2p^1\Sigma$ with other $^1\Sigma$ levels of the proper symmetry type. However, for the evaluation of this correction a more detailed knowledge of the energy states and wavefunctions is necessary than is available now. We do not think that the omission of this term accounts for the big discrepancies which will remain.

The corrections Δ_a and Δ_b are found to be

	H₂	HD	D₂
Δ_a	−2.396	−1.556	−0.846
Δ_b	−2.454	−1.562	−0.858

The correction Δ_b is implied in the Y_{10} values given in the Table VIII, as the extra term $2B_V$ in the energy which is responsible for the correction was regarded as belonging to the rotational energy and subtracted before the vibrational differences were evaluated. The application of (7) will make the agreement between the isotopic ratios and the theoretical values better, but the discrepancies are still considerable.

A large part of this discrepancy will be due to the fact that the expression (3) used for the calculation of the constants converges so badly that the neglected higher terms may be important enough to falsify the results. If that were the only source of errors we might try to obtain better values of the vibrational constants by making use only of the levels with $V=0$ and 1 for which (3) converges best and the influence of the higher terms is negligible, and make use at the same time of the isotopic relations between the constants. We would have then

$$\omega - 2x + 3.25y - 5z = 1322.694,$$
$$\rho_{12}\omega - 2\rho_{12}{}^2x + 3.25\rho_{12}{}^3y - 5\rho_{12}{}^4z = 1150.15,$$
$$\rho_{13}\omega - 2\rho_{13}{}^2x + 3.25\rho_{13}{}^3y - 5\rho_{13}{}^4z = 943.917,$$
$$\rho_{13}\omega - 4\rho_{13}{}^2x + 12.25\rho_{13}{}^3y - 34\rho_{13}{}^4z = 924.319,$$
$$(8)$$

in which the right sides are the first vibrational differences with the Δ_a and Δ_b corrections applied.

Unfortunately the solution of these equations gives values for the constants which seem quite impossible, from which we can conclude that the neglected interaction terms are sufficiently big to make themselves felt. Although, therefore, Eqs. (8) cannot be used in this case to obtain better values for the vibrational constants, they serve as a test for the reliability of these constants. In our case this test must be considered negative, showing that the true vibrational constants may be considerably different from those obtained by the conventional methods.

The ratios of the other vibrational constants deviate even more from their theoretical values than those of Y_{10}. The discrepancy is more than 5 percent for Y_{20} and more than 60 percent for Y_{30} and Y_{40}. Various corrections should be applied, but most of these corrections are even more uncertain than those for Y_{10} and therefore it seems futile to try to apply tham at the present stage.

§4. THE $3d^1\Pi^-$ STATE

The $3d^1\Sigma$ and $3d^1\Pi$ levels show the phenomenon of L decoupling to such a degree that the quadratic formula (1) for the rotational energy is no more a good first approximation. The formulae for the rotational energy if the L decoupling is taken into account are much more complicated,[14] and very disagreeable to handle for the computation of the constants. Furthermore we must expect that there are perturbations, which it would be difficult to recognize as we do not have a simple expression for the unperturbed levels. The reason for expecting the perturbations is that Richardson and Davidson[1] discovered in the vicinity of the $3d$ state a number of other electronic levels the origin of which is not completely cleared up yet, but which in all probability must have both electrons excited.[15] All these levels give rise to P and R branches when they combine with the $2p\Sigma_u^+$ state which proves that they must be even and plus levels[16] and they must be able to

perturb the $3d^1\Sigma^+$ and $3d^1\Pi^+$ states but not the $3d^1\Pi^-$ levels. Whereas this fact makes it very likely that the $3d^1\Sigma$ and $3d^1\Pi^+$ states will show perturbations, it proves by no means that $3d^1\Pi^-$ is free of them. There may be minus levels which can perturb $3d^1\Pi^-$ but as long as they have not been discovered it seems worth while to go out from the assumption that $3d^1\Pi^-$ is free from perturbations and try to calculate the constants.

If we start out with Van Vleck and Hill's model of an atom with rigidly connected nuclei and an orbital angular momentum $L = 2$ which is loosely coupled to the internuclear axis[14, 17] the rotational energy turns out to be the root of a quadratic secular equation

$$W(J) = B[J(J+1)+1]+5A/2 \\ -[(2J+1)^2B^2-9AB+9A^2/4]^{\frac{1}{2}}. \quad (9)$$

When we apply this formula to the empirical data we must realize that it applies to rigidly connected nuclei only. For the vibrating molecule because of the much higher frequency of the vibrations compared with the rotational frequency, a similar formula will hold; only the constants are now certain averages over all the positions of the nuclei during a vibration and therefore functions of the vibrational quantum number V.

If (9) is to be applied to the empirical data it is necessary to take into account the effect of the distortion of the molecule due to the centrifugal

[14] G. H. Dieke, Zeits. f. Physik **57**, 71 (1929).

[15] W. Weizel, Zeits. f. Physik **65**, 456 (1930); O. W. Richardson, *Molecular Hydrogen and Its Spectrum*.

[16] It is very unfortunate that the nomenclature of the symmetry properties is in a rather confused state. The wave functions which are multiplied by a factor $+1$ or -1, respectively, with a reflection of the electrons at the origin are called even (g) and odd (u), but positive and negative if all the particles are reflected (Wigner and Witmer, Weizel, Mulliken). Others (Kronig, Pauling and Wilson) call them even and odd in both cases, and that seems preferable to us, as it is the same property and the designation positive and negative becomes available to characterize the behavior if the sign of the azimuth φ about the internuclear axis is changed (reflection at the ξ ζplane). It seems unnatural to have to avoid the words positive and negative in connection with symbols like Σ^+ and Σ^- which are universally used to express this property. Therefore it seems only natural to express the same property for the sublevels of a Π state by Π^+ and Π^-. These levels are now often called Π_c and Π_d but there seems to be little need for this rather arbitrary designation and we believe that all confusion can be avoided if we call Σ^+, Π^+ etc. states plus states and the Σ^-, Π^- etc. minus states and avoid the words positive and negative, the use of which seems not yet to be generally agreed upon. We may remind the reader of the fact that for a plus state the rotational levels with even values of J are even and those with odd values of J odd. This applies to all diatomic molecules whether the nuclei are identical or not.

[17] E. L. Hill and J. H. Van Vleck, Phys. Rev. **32**, 250 (1928).

TABLE X. *Constants of $3d^1\Pi^-$*.

	H$_2$	HD	D$_2$		H$_2$	HD	D$_2$
B_0	29.03	21.75	14.475	A_0	153.8	150.3	148.0
B_1	27.52	20.52	13.95	A_1	184.6	181.0	168.3
B_2	26.00	19.34	13.42	A_2	220.5	224.0	191.8
B_3		18.11	12.90	A_3		299.7	217.7
B_4		18.00	12.51	A_4		240.1	219.5
D_0	0.013	0.007	0.0025	ω_{10}	2108.29	1845.72	1523.64
D_1	0.14	.0045	.0030	ω_{21}	1951.36	1729.30	1447.14
D_2	0.14	.004	.0033	ω_{32}	1781.68	1605.04	1367.41
D_3		.004	.0035	ω_{43}		1461.59*	1280.45
D_4		.005	.0037				
Ae	136.3	127.3	136.5				
Be	29.790	22.36	14.739	Y_{10}	2265.22	1962.14	1600.14
Y_{11}	1.515	1.21	0.526	Y_{20}	78.47	58.21	39.42

forces of the rotation. If the decoupling can be neglected the effect on the energy is

$$-DJ^2(J+1)^2.$$

If on the other hand the decoupling is practically complete this term becomes

$$-D(J-1)^2J^2.$$

For intermediate decouplings it will lie between these two values. But as we are here dealing only with a small correction term and because of the approximate character of the calculations it is sufficiently accurate to take the first expression throughout.

The evaluation of the constants can be done most conveniently in the following way. We note that $W(1) = A + 6B$. The differences $W(J) - W(1)$ can be obtained from the frequencies of the lines of the Q branches and the known values for the corresponding differences of the $2p^1\Sigma$ state. It is now necessary to find such values for the constants A, B and D that

$$W(J) - W(1) = 3A/2 + B[J(J+1) - 5]$$
$$- [(2J+1)^2B^2 - 9AB + 9A^2/4]^{\frac{1}{2}}$$
$$- D[J^2(J+1)^2 - 4] \quad (10)$$

for all values of J except the higher ones for which other terms neglected here might become important. As the expression (10) is too complicated for any of the standard methods of evaluating constants, the best way is a systematic method of trial and error. Table X gives the results of these calculations. The first question is whether (9) or (10) represent the actual energies with sufficient approximation. This can be

answered by a study of Table XI in which the empirical values for $W(J) - W(1)$ are given and their differences with the calculated values. It can be seen that the agreement is quite good except for a few of the highest J values. For D$_2$ the agreement is within the limits of experimental errors for all values of J up to 6. For HD the agreement is less good and that is probably due to the fact mentioned and explained previously that on the whole the data for HD are not as accurate and reliable as those for H$_2$ and D$_2$.

While it is thus established that a formula of the type (10) represents well the empirical energy levels, we must not expect that it will be able to give account of all the fine details, as the interaction between vibration and rotation and electronic motion is inadequately taken care of.[18] We shall see, however, that even with the approximate treatment the main features of all the constants are as they must be expected for a level of this type.

The constant A expresses the degree of coupling of the orbital angular momentum to the internuclear axis. If the angle between internuclear axis and orbital momentum is α the coupling energy for a d electron is

$$4A \cos^2 \alpha.$$

A is a measure for the departure from central

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[18] At the symposium on molecular structure of the Physical Chemistry Section of the American Chemical Society in Princeton on January 1, 1937 an account was given in which this interaction was properly treated. As however not all the details of these calculations are completely finished, we reserve the application of these formulae to the energy levels under discussion to a future paper.

symmetry. It would be zero if the two nuclei coincide and increases with increasing internuclear distance. If the molecule vibrates, the average internuclear distance is larger than for the nonvibrating molecule, which means that the value of A should increase with increasing vibrational quantum numbers. That is exactly what happens, as Table X shows. Also in agreement with the expectations is the fact that A increases less rapidly for D_2 than for H_2, as for a given quantum number V the amplitudes are biggest for H_2 and smallest for D_2. The variation of A with V is roughly linear.[19]

We can extrapolate to the vibrationless molecule and find the values listed under A_e in Table X. They should be the same for the three mole-

cules as the coupling is not influenced by the masses of the nuclei. The agreement is very good for H_2 and D_2. The value for HD is not unreasonably off, as the possible error in the determination of the A_V values is considerable.

The values of B_V decrease approximately linearly with V, as is the case in general for diatomic molecules. The agreement of the ratios of B_e for the three molecules 0.7506, 0.4948 and 0.6592 with the theoretical values 0.7502, 0.5004 and 0.6670 is not very good, which shows the limitations of expression (9).[20]

Not much reliance can be put on the values of D_V in Table XI, although they seem fairly consistent.

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[19] The value A_4 for D_2 seems to be abnormal. The reason for this is not clear. There may possibly be a small perturbation.

[20] Corrections similar to those in §3 should be applied to B_e, ω_e etc. but their influence will be small compared with the much larger discrepancies observed and therefore it would be futile to apply them.

TABLE XI. *Observed rotational levels of $3d^1\Pi^-$ and the differences between the observed and calculated levels.*

J	$V=0$	diff.	1	diff.	2	diff.	3	diff.	4	diff.
					H_2					
1	0		0		0		0			
2	74.71	0.00	80.73	0.00	83.10	0.00	77.19			
3	199.19	−.02	206.98	.00	209.59	0.05	201.39			
4	376.22	−.01	380.83	−.04	380.30	.07	367.08			
5	606.20	.01	602.96	−.06	595.31	−.07	573.99			
6	888.31	.01	873.16	−.20	854.46	−.01				
7			1189.45	.08	1156.17	−.11				
					HD					
1	0		0		0		0		0	
2	64.73	0.00	66.52	0.02	66.76	0.01	65.78	0.02	63.85*	0.32
3	165.68	−.03	167.78	−.01	167.26	−.06	164.30	−.06	158.39*	−.54
4	304.90	.10	304.94	.00	302.03	−.02	295.67	−.05	285.76*	−.46
5	483.18	.10	478.75	.07	471.29	.07	459.81	.07		
6	700.27	.18	688.94	−.42						
7	955.62	−.36	937.27	.30						
8	1249.72	−.06								
					D_2					
1	0		0		0		0		0	
2	48.69	0.00	48.46	0.00	47.85	0.01	46.95	0.02	45.74	0.05
3	122.35	.00	121.40	.01	119.62	−.03	117.20	.04	114.12	.00
4	221.49	.01	219.02	−.02	215.33	−.10	210.68	−.05	205.02	−.11
5	346.56	.07	341.54	.05	335.14	.01	327.46	−.07	318.45	−.08
6	497.55	−.06	488.84	.03	478.68	.05	467.06	−.03	453.91	−.11
7	674.49	−.42	660.87	−.05	645.92	.21			611.50*	.27
8					836.51	.45				
9					1049.64*	−.40				

* Uncertain.

§5. The Vibrational Constants of $3d^1\Pi^-$

The vibrational differences can be best obtained from the $Q(1)$ lines. By subtracting e.g., $Q(1)$ of $1{\to}V''$ and $0{\to}V''$ the E_1-E_0 differences are obtained. They still contain a part of the rotational energy as from (9) it follows that $W(J)=A+6B$ for $J=1$. The differences $6(B_0-B_1)$, $6(B_1-B_2)$ etc. must be added therefore to the differences in the table to obtain the real vibrational differences from which the constants occurring in (3) can be evaluated. The average values of all these differences are listed in Table X.

The data are sufficient only for D_2 to calculate the four constants Y_{10}, Y_{20}, Y_{30}, Y_{40}. They are

$$Y_{10}=1600.73, \qquad Y_{20}=-39.42,$$
$$Y_{30}=0.796, \qquad Y_{40}=-0.167.$$

In order to obtain the constants for H_2 and HD for which only three differences are known, we might take Y_{40} of D_2 divide it by $\rho_{13}{}^4$ and $\rho_{23}{}^4$ respectively, and then calculate the three other constants from the observed differences. Such a procedure is, however, not very advisable on account of the poor convergence of the series (3) to which attention has already been drawn in §3.

For H_2 the series would be for $V=3$ and $V=4$ if the constants given above for D_2 are correct

$$W_3=7928.27-961.26+96.43-100.05,$$
$$W_4=10193.49-1589.02+204.94-272.47.$$

From the behavior of the successive terms we see that we cannot expect the omitted higher terms to be so small that they are negligible. Any attempt to calculate the constants from a series with such poor convergence would be liable to very considerable errors and some of the constants would probably be entirely meaningless.

For this reason it is better to give up entirely the attempt to find the values of Y_{30} and Y_{40} and to restrict ourselves to finding the values of Y_{10} and Y_{20} from the first two differences only. Those values are listed in Table X.

The values of the isotopic ratios of these constants with their theoretical values in brackets are

$Y_{10}.0.86620$ (0.86613) 0.70640 (0.70737) 0.81551 (0.81670)
Y_{20} 0.7418 (0.7502) 0.5024 (0.5004) 0.6772 (0.6670).

There are big deviations which show that the values of Y_{10} and Y_{20} must have considerable errors.

One can adopt a procedure similar to the one proposed in §3 by making use of the first differences of HD and D_2 only which will have the smallest errors.

From

$$Y_{10}+2Y_{20}=1845.72$$
$$\rho_{23}Y_{10}+2\rho_{23}{}^2Y_{20}=1523.64$$

we obtain the constants Y_{10} and Y_{20} for HD. By multiplying them with the appropriate isotopic factors those for the two other molecules are found. They are

TABLE XII. *Origins of bands $3d^1\Pi{\to}2p^1\Sigma$.*

V' \ V''	0	1	2	3	4	5	6	7	8	9
					HD					
0	21684.97	20536.38	19416.16	18322.70	17255.18					
1	23530.69	22382.10	21261.88	20168.42	19100.90	18058.69				
2	25259.99	24111.40	22991.18	21897.72	20830.20	19787.90	18770.12	17776.70		
3	26865.03	25716.44	24596.22	23502.76	22435.24	21392.96	20375.18	19381.76	18413.01	
4				24964.36		22854.54	21836.76	20843.34	19874.59	
					D_2					
0	21624.30	20681.26	19757.78	18852.65	17964.98	17094.54				
1	23147.98		21281.38	20376.20	19488.60	18618.11				
2	24595.09	23652.03	22728.56	21823.23	20935.51	20065.26	19211.63	18374.56		
3	25962.52	25019.45	24095.94	23190.75	22303.16	21432.65	20579.03	19742.00	18921.31	18116.85
4		26299.89	25376.37	24471.23	23583.54	22712.63		21022.45	20201.78	19397.33

	H$_2$	HD	D$_2$
Y_{10}	2256.28	1954.23	1596.02
$-Y_{20}$	72.32	54.26	36.73

and differ considerably from the values in Table X. We are inclined to believe that these values are better but as we saw in §3 that this method is not free from objections, we cannot be sure. We see here again that we cannot expect to obtain very accurate values for the vibrational constants of the hydrogen molecule which have the theoretical significance they are supposed to have.

Table XII gives the zero lines of all the observed bands. The contribution

$$[L(L+1) - \Lambda^2]B_V$$

to the energy[17, 13, 21] has been regarded as belonging to the rotational energy, and the zero lines are defined as transitions between the rotationless molecule.

By adding and subtracting respectively the vibrational energies of the final and initial states we obtain as the origins of the band systems

H$_2$	HD	D$_2$
21295.22	21304.06	21312.68

These three values should be identical except for some small interaction terms. The term

$$[L(L+1) - \Lambda^2]B_V$$

discussed previously[21] has been taken into account so that the remaining discrepancy must be due to the other more uncertain terms.[13]

§6. THE $3d^1\Sigma$ AND $3d^1\Pi^+$ STATES

In the preceding paragraphs it was shown that the regular L decoupling is sufficient to account for the structure of the $3d^1\Pi^-$ level, and that there is no positive evidence for perturbations. For the $3d^1\Sigma$ and $3d^1\Pi^+$ states, however, the situation is different. We know[14] that the rotational energy of $d^1\Sigma$ should be for $J=0$ equal to $6B$, whereas the rotational energy of $d^1\Pi^-$ for $J=1$ is equal to $A+6B$. The difference between these two levels should, therefore, be equal to the constant A. Whereas for the actual molecule we

cannot expect this relation to hold exactly, it should be right at least approximately even for the nonrigid molecule. We find this difference empirically to be 260.25 for H$_2$, 293.76 for HD, and 258.21 for D$_2$, whereas A_0 was found above to be about 150. If we accept the assumption that the $3d^1\Pi^-$ level is free from perturbations we are led to the conclusion that the $3d^1\Sigma$ levels are shifted more than 100 cm^{-1} from their expected positions. That this shift is due at least partly to perturbations is supported by the fact that the difference for HD is more than 33 cm^{-1} bigger than that for H$_2$ and D$_2$. If a more systematic cause were responsible for it we would expect the value for HD to lie between that of H$_2$ and D$_2$. Moreover, we can calculate the rotational levels of $3d^1\Sigma$ and $3d^1\Pi^+$ by solving the cubic secular equation with the values of A and B obtained from the $3d^1\Pi^-$ level. If we do so, we find that the rotational levels obtained in this way do not agree at all with those empirically found. This proves again that both the $3d^1\Sigma$ and $3d^1\Pi^+$ states are abnormal.

It was mentioned before that the source of the perturbations is probably one or more of the numerous extra levels found by Richardson and Davidson in this region. The nature of the perturbations is in agreement with this. All the extra levels identified with any dgree of certainty are $^1\Sigma_g^+$ levels. Their interaction with the $3d^1\Sigma_g^+$ states would give rise to type B perturbations[22] which are due to vibrational coupling, and for which also the rotationless levels, i.e., the vibrational levels are perturbed. That is exactly what is observed, for the shift of the whole $V=0$ level by more than 100 cm^{-1} from its expected position can only be explained by class B perturbations. Class B perturbations give rise for the same reason to irregular vibrational intervals. This is shown by the following table which gives the vibrational differences for $J=0$, or $J=1$ when the $J=0$ level is not known. In the latter case the value is marked by an asterisk.

	H$_2$	HD	D$_2$
ω_{10}	2232.02	1879.93	1440.83
ω_{21}	2120.21	1896.39	
ω_{32}	1744.68*	1899.02	

[21] G. H. Dieke, Phys. Rev. 47, 661 (1935).

[22] G. H. Dieke, Phys. Rev. 47, 870 (1935).

We see that for H_2 and HD the first two differences are larger than the corresponding differences of the $3d^1\Pi^-$ level, whereas for D_2 just the opposite is true. For H_2 the differences decrease rapidly with increasing V for HD they increase. This can happen only when there are marked anomalies of the vibrational levels. For the D_2 molecule the vibrational levels with $V>1$ could not be found, and certainly are not in or near the expected position with anything like the expected intensity. Very likely a strong perturbation is the cause for that.

While the perturbations of the $3d^1\Sigma$ state are found to be of class B, those of $3d^1\Pi^+$ should be of type A, because the values of Λ of the perturbing and perturbed states differ by one. Class A perturbations are due to the interaction of rotation and electronic motion and therefore should be absent for the rotationless molecule. That is found to be the case, for if one extrapolates the $3d^1\Pi^+$ levels to the rotationless state they coincide with the rotationless $3d^1\Pi^-$ levels with the accuracy to which such an extrapolation is possible. (See Table XIII.) However, the actual differences between $3d^1\Pi^+$ and $3d^1\Pi^-$ rotational levels (Λ doubling) vary quite irregularly with the vibrational quantum number which shows again that if $3d^1\Pi^-$ is normal $3d^1\Pi^+$ must have irregularities.

With the presence of perturbations thus established, there is no point in trying to calculate the rotational and vibrational constants of $3d^1\Sigma$ and $3d^1\Pi^+$. An accurate evaluation of the rotational constants would be even much more cumbersome than for the $3d^1\Pi^-$ state as no workable formula for the rotational energy can be given. The rotational levels can only be found as the roots of a fairly complicated secular equation.

§7. OTHER BAND SYSTEMS

Tables V and VI give bands ending on the $2p^1\Sigma$ level which originate from unclassified upper states. They are analogous to the extra levels which Richardson and Davidson found for H_2 and to which we have referred previously. However we have not yet been able to find these extra levels for HD and D_2 with nearly the same com-

TABLE XIII. Λ *doubling of* $3d^1\Pi$.

J	$V=0$	1	2	3
		H₂		
1	62.33	51.82	39.34	53.22
2	134.63	100.89	151.62	63.15
3	198.95	123.38	171.04	50.97
4	254.58	124.69	180.20	3.57
		HD		
1	38.05	29.11	40.84	39.45
2	91.61	62.24	64.94	46.34
3	146.51	94.80	133.13	128.11
4	195.40	116.94	193.98	197.40
5	238.42			
6	274.08			
7	317.54			
		D₂		
1	18.75	9.77	9.49	
2	49.30	26.16	22.55	
3	85.18	45.00	35.85	
4	122.06	58.21	44.99	
5	156.95	82.32		
6	190.27			
7	218.06			

pleteness as they were found in H_2. Also the identification of these lines is not of the same degree of reliability as for the bands in Tables I–IV. Therefore we restrict ourselves to merely listing these bands without trying to find an interpretation for them. For their ultimate classification the facts of the preceding paragraph seem to be significant, namely that from the perturbations of the $3d^1\Sigma$ and $3d^1\Pi$ levels there is no evidence that there are in this region other than Σ^+ levels,[23] which is very curious as almost any electron arrangement should also give other types of states.

There are also some HD bands originating from $3d^1\Delta$. These bands are also weak and incomplete as the $\Delta\rightarrow\Sigma$ transition is ordinarily forbidden and made possible only by the Λ decoupling in the $d\Delta$ state.

We wish to thank Mr. W. Durding for his help with some of the calculations.

[23] Richardson's λ4142.8 progression seems to be an exception, as it seems to consist of Q branches only. However, whether these branches are actually Q branches or perhaps disguised R branches is difficult to decide without more knowledge about the bands.