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The Near Infra-Red Spectrum of Water Vapor

Part I. The Perpendicular Bands ν_2 and $2\nu_2$

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The rotation-vibration bands in the water vapor spectrum lying in the bolometric infra-red have been completely remeasured. In this paper the measurements are reported on the bands ν_2 and $2\nu_2$. An analysis of the complicated rotational structure has been carried out. From the interpretation of the data the value of the normal frequency ν_2 and the anharmonic constant U_{22} have been calculated as well as the values of the moments of inertia effective in these two vibration states. The frequency ν_2 is found to take the value 1653.8 cm^{-1} and the anharmonic constant $U_{22} = -19.25$ cm^{-1}. For the states ν_2 and $2\nu_2$ the effective moments of inertia take the values $I_x^{(e)} = 0.905 \times 10^{-40}$ g cm^2, $I_y^{(e)} = 1.902 \times 10^{-40}$ g cm^2, $I_z^{(e)} = 3.054 \times 10^{-40}$ g cm^2 and $I_x^{(e)} = 0.775 \times 10^{-40}$ g cm^2, $I_y^{(e)} = 1.895 \times 10^{-40}$ g cm^2, $I_z^{(e)} = 3.095 \times 10^{-40}$ g cm^2, respectively. The values arrived at for the above constants serve to confirm the theory of the water vapor molecule.

I. INTRODUCTION

THE infra-red spectrum of water vapor has probably been studied more extensively than that of any other molecule. High dispersion measurements had been made by Sleator[1] already in 1918 and by Sleator and Phelps[2] in 1925 and while their resolution was insufficient to permit a rotational analysis, they did serve to reveal the character of the bands and facilitated their identification. So many bands have been measured and identified in the water vapor spectrum that after a detailed study of the vibration problem, Bonner[3] was able to evaluate the harmonic and anharmonic constants of the potential energy of the molecule with considerable accuracy. An attempt to analyze the rotational structure was first made by Mecke[4] who successfully identified many lines in the bolometric bands remeasured by Plyler and Sleator[5] and in the bands in the photographic infra-red. Mecke did not compensate for the centrifugal stretching of the molecule in his work so that his assignment of lines can be considered reliable only in cases when the transitions are between levels where the quantum number of total angular momentum, J, has small values.

The most convincing progress toward a satisfactory interpretation of the water vapor spectrum is contained in two recent papers, one by Randall, Dennison, Ginsburg and Weber[6] and the other by Darling and Dennison.[7] The first of these deals with high dispersion measurements on the pure rotation spectrum of water vapor. The authors have identified nearly all the observed lines with quantum transitions made by the molecule between the rotation energy levels associated with the normal vibration state. It has thus been possible for them to deduce the values of rotation energy levels in this vibration state. The second paper is essentially a re-evaluation of the vibration-rotation data for the molecule which has enabled the writers to assign values to the moments of inertia effective in many vibration states and to evaluate the constants of the potential energy function. In general, the results are consistent with the theory for nonlinear triatomic molecules as first set forth by Shaffer and Nielsen[8] and subsequently verified by these authors, that the effective moments of inertia are, to the second

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[1] W. W. Sleator, Astrophys. J. **48**, 125 (1918).

[2] W. W. Sleator and E. R. Phelps, Astrophys. J. **62**, 28 (1925).

[3] L. G. Bonner, Phys. Rev. **46**, 485 (1934).

[4] R. Mecke, Zeits. f. Physik **81**, 313 (1933).

[5] E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1433 (1931).

[6] H. M. Randall, D. M. Dennison, N. Ginsburg and L. R. Weber, Phys. Rev. **52**, 160 (1937).

[7] B. T. Darling and D. M. Dennison, Phys. Rev. **55**, 128 (1940).

[8] W. H. Shaffer and H. H. Nielsen, Phys. Rev. **56**, 188 (1939).

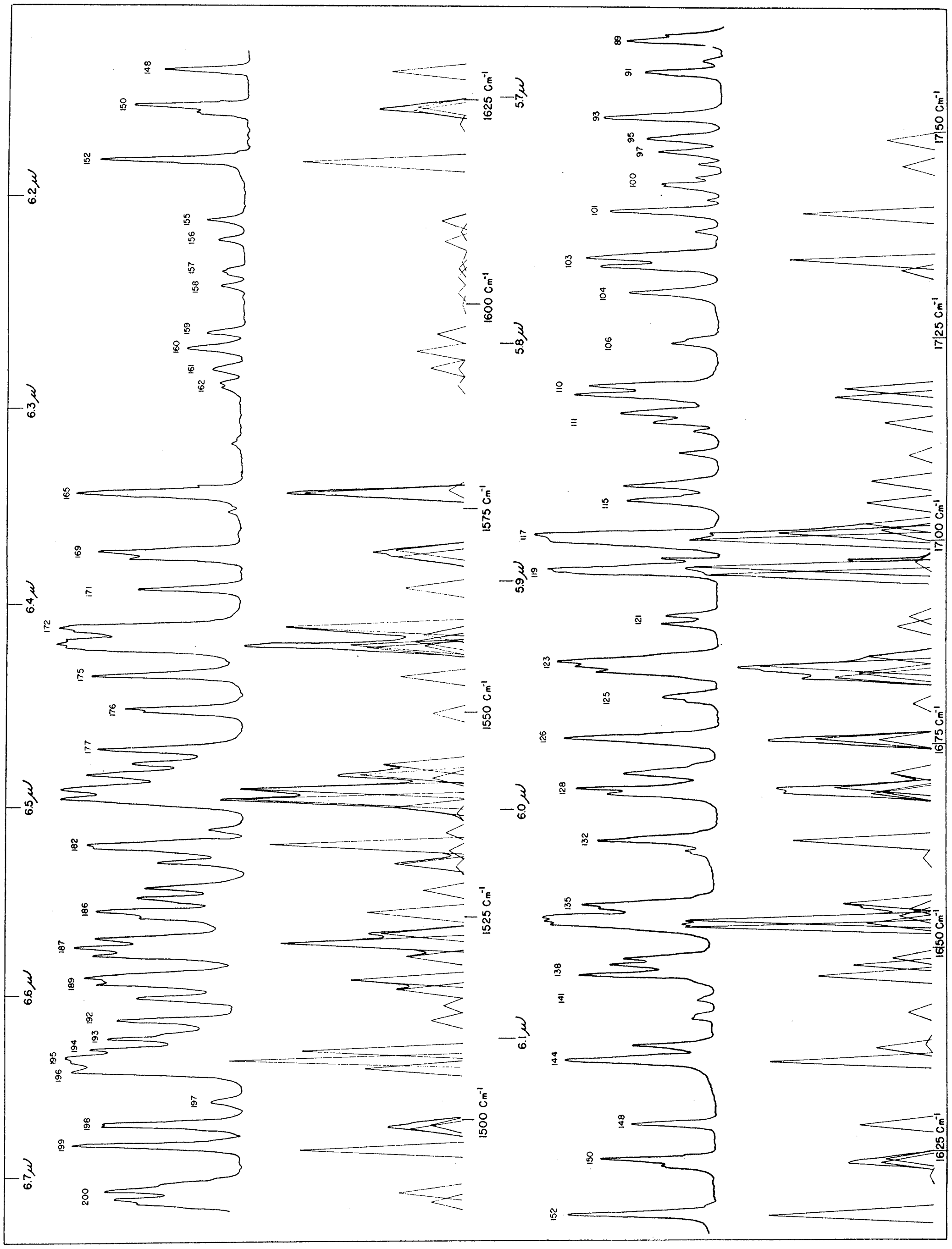

FIG. 1. Rotation vibration lines in the 6.26μ water vapor band.

order of approximation, linear relations of the vibration quantum numbers.

The bands for which the rotational analysis has been least convincing are the ones lying in the region from 1.5μ to 7.0μ. A principal reason for this is that, when measurements have been made, at least in the case of the fundamental bands, far too much water vapor has been present. This condition has prevailed because it has been necessary to make the measurements

TABLE I. *Rotation-vibration lines in the 6.26μ water vapor band.*

LINE No.	ν OBS.	ν CALC.	TRANSITION
200(*a*)	1490.0	1490.0	$6_{-5}-6_{-3}$
(*b*)	1491.1	1491.1	$4_{-4}-5_{-4}$
199	1496.2	1496.1	$4_{-3}-5_{-5}$
198(*a*)	1499.2	1499.2	1_0-2_2
(*b*)	1499.4*	1500.2	$6_{-6}-6_{-4}$
197	1502.1		?
196	1505.8		?
195(*a*)	1506.6	1506.4	$5_{-4}-5_{-2}$
			1_1-2_1
(*b*)	1507.5	1507.5	$3_{-3}-4_{-3}$
194	1508.6	1508.6	$4_{-1}-5_{-3}$
193	1509.8		?
		1512.6	5_3-5_5
		1512.9	6_2-6_4
192	1512.4	1512.2	6_1-6_3
		1512.8	$6_{-3}-6_{-1}$
		1512.6	$5_{-3}-4_3$
191	1514.9	1514.8	6_3-6_5
190	1516.5	1516.5	5_0-5_2
189	1517.4	1517.0	4_1-4_3
		1517.8	$3_{-2}-4_{-4}$
188	1520.1	1520.0	5_1-5_3
		1520.3	$5_{-2}-5_0$
187(*a*)	1521.2	1521.0	$4_{-3}-4_{-1}$
		1521.2	$5_{-5}-5_{-3}$
(*b*)	1523.1	1523.9	5_0-6_{-2}
		1523.2	$2_{-2}-3_{-2}$
186	1525.6	1525.6	$4_{-1}-4_1$
185	1527.2		?
184	1528.7	1528.8	3_0-3_2
183	1531.5	1532.3	$4_{-4}-3_2$
		1531.3	6_0-6_2
182(*a*)	1533.2	1533.4	$3_{-2}-3_0$
(*b*)	1533.9	1534.0	3_1-3_3
(*c*)	1535.5	1535.1	$6_{-4}-6_{-2}$
		1538.9	3_0-4_{-2}
181	1539.2	1539.2	$1_{-1}-2_{-1}$
		1539.5	4_0-4_2
		1539.1	$6_{-6}-5_0$
180	1540.5	1540.4	$2_{-1}-3_{-3}$
179	1542.3	1542.3	$2_{-1}-2_1$
		1542.4	$4_{-4}-4_{-2}$
178	1543.6	1543.5	$5_{-1}-5_1$
177	1545.3		?
176(*a*)	1549.8	1549.9	$6_{-2}-6_0$
(*b*)	1550.3		?
175	1554.4	1554.3	$5_{-3}-5_{-1}$
174(*a*)	1557.9	1558.1	2_0-2_2
(*b*)	1558.3	1558.3	6_1-7_{-1}
			0_0-1_0
(*c*)	1558.9	1558.7	4_1-5_{-1}
		1558.9	$3_{-3}-3_{-1}$
173	1559.6	1559.6	$4_{-2}-4_0$
172	1560.3	1560.5	$3_{-1}-3_1$
171	1565.1	1565.3	1_0-2_{-2}
169	1569.0*	1569.2	2_1-3_{-1}
168	1569.8*	1570.4	$2_{-2}-2_0$
165(*a*)	1574.8		
(*b*)	1576.2	1576.3	$1_{-1}-1_1$
162(*a*)	1589.6		
(*b*)	1590.4	1590.6	4_2-5_{-2}
161	1592.3	1592.0	5_2-6_0
		1592.3	3_2-4_0
160	1594.7	1594.8	3_1-4_{-3}
		1596.5	$6_{-5}-5_{-1}$
159	1596.7	1596.9	4_0-5_{-4}
158	1601.6	1601.6	2_2-3_{-2}
157	1603.7	1603.6	$3_{-2}-2_2$
156	1607.8	1607.8	3_3-4_{-1}
155	1610.2	1610.3	5_3-6_{-1}
152	1617.4	1617.4	1_1-1_{-1}
150	1623.3	1623.3	4_3-5_1
149	1624.2	1624.2	2_0-2_{-2}
		1628.3	4_4-5_0
148	1628.3	1628.3	$2_{-2}-1_0$
		1628.6	6_3-7_1
144	1636.0	1635.3	1_0-0_0
		1635.9	$3_{-1}-3_{-3}$
143	1638.3	1637.8	$3_{-1}-2_1$
		1638.1	4_0-3_2
		1638.5	5_0-4_4
142	1641.2	1642.2(*W*)	5_1-4_3
141	1643.7		?
139	1646.3	1646.2	3_1-3_{-1}
138	1648.1	1648.2	4_0-4_{-2}
137	1648.6	1648.8	2_2-2_0
		1652.8	$3_{-3}-2_{-1}$
136(*a*)	1653.0*	1652.9	$5_{-1}-5_{-3}$
		1653.0	$6_{-3}-5_1$
(*b*)	1653.5*	1653.3	$2_{-1}-1_{-1}$
(*c*)	1653.9*	1653.4	$4_{-2}-4_{-4}$
(*d*)	1654.4	1654.5	5_4-6_2
135(*a*)	1654.9		
(*b*)	1655.4	1655.4	5_5-6_1
133	1661.7*(*W*)	1660.2	$6_{-1}-5_3$
132	1663.2	1633.1	2_1-2_{-1}
129	1669.0	1668.7	$6_{-2}-6_{-4}$
		1669.0	$4_{-2}-3_0$
128	1669.6	1669.7	$3_{-2}-2_{-2}$
		1669.9	$5_{-1}-4_1$
127	1671.5	1671.9	3_0-3_{-2}
126	1675.6	1675.4	$4_{-4}-3_{-2}$
		1675.6	$5_{-3}-5_{-5}$
125(*a*)	1680.1	1680.0	4_1-5_{-5}
(*b*)	1680.8	1680.0	5_0-6_{6}
(*c*)	1681.6		
123	1683.5	1683.4	$4_{-1}-4_{-}$
		1683.9	5_1-5_{-1}
122(*a*)	1684.6*	1684.6	$4_{-3}-3_{-3}$
		1684.3	$6_{-1}-7_{-7}$
(*b*)	1686.1	1686.1	3_2-4_{-4}
		1686.3	6_0-6_{-2}
121	1689.9	1690.7	6_5-7_3
120	1690.9	1690.9	4_2-4_0
		1691.1	6_6-7_2
		1691.2	$6_{-4}-6_{-6}$
			3_3-3_1
119(*a*)	1696.0	1696.0	$5_{-5}-4_{-3}$
(*b*)	1696.4	1696.6	6_1-7_{-5}
118	1697.8	1697.7	$5_{-2}-5_{-4}$
117(*a*)	1700.5	1700.1	2_1-1_1
		1700.5	$5_{-4}-4_{-4}$
			$5_{-3}-4_{-1}$
(*b*)	1701.8	1701.7	3_2-3_0
115	1704.9	1704.9	4_1-4_{-1}
114	1706.7	1706.7	2_2-1_0
		1707.6	$6_{-2}-5_0$
113	1710.8	1710.7	5_0-5_{-2}
		1710.8	5_2-6_{-4}
112(*a*)	1713.6		?
(*b*)	1714.6	1714.6	$6_{-3}-6_{-5}$
111	1715.8*W*		?
110(*a*)	1717.8	1717.6	$6_{-1}-6_{-3}$
		1717.8	$6_{-5}-5_{-5}$
(*b*)	1718.9	1718.9	3_0-2_0
106	1724.2		?
104	1730.4		?
103(*a*)	1733.6	1732.8	4_3-5_{-3}
(*b*)	1734.6	1734.8	$4_{-1}-3_{-1}$
102	1737.8		?
101	1740.2	1740.1	3_1-2_{-1}
		1740.2	6_2-6_0
100	1743.2		?
99	1744.4		?
98	1746.0	1746.0	5_3-5_1
97	1747.5		
		1748.9	$5_{-2}-4_{-2}$
95	1749.6	1749.7	5_2-5_0
		1749.7	4_3-4_1
93	1751.6	1751.9	6_1-6_{-1}
91	1757.1		?
90	1758.7		?
89(*a*)	1762.1		?
(*b*)	1762.7		?

* Lines marked with an asterisk are components of a group of very close-lying lines. In such cases the frequency positions of the individual components may be slightly in error.

(*W*) The character (*W*) after a line indicates that it is a line of small intensity. In certain such cases the actual frequency position may be slightly in error.

TABLE II. *Rotation-vibration lines in the 3.3μ water vapor band.*

LINE No.	ν OBS.	ν CALC.	TRANSITION
103–*a*	3011.5	3011.2	3_1-4_1
103–*b*	3013.8		?
103–*c*	3014.6		?
102–*a*	3016.8		?
102–*b*	3017.7	3017.6	$6_{-6}-7_{-6}$
102–*c*	3018.8	3018.7	$6_{-5}-7_{-7}$
102–*d*	3019.5		?
101–*a*	3023.7	3023.3	3_2-4_4
		3023.5	3_3-4_3
101–*b*	3025.9	3026.2	6_4-7_4
			6_3-7_5
101–*c*	3027.1	3026.9	$2_{-1}-3_1$
101–*d*	3028.6	3028.3	4_3-5_5
		3028.3	4_4-5_4
101–*e*	3030.0		?
100	3032.2	3032.8	$5_{-5}-6_{-5}$
		3033.0	$6_{-3}-7_{-5}$
99	3033.9	3034.4	2_1-3_3
98–*a*	3035.8	3035.0	$3_{-1}-4_{-1}$
		3035.8	2_2-3_2
98–*b*	3037.4	3037.0	$5_{-4}-6_{-6}$
98–*c*	3038.9		?
98–*d*	3040.3		?
98–*e*	3043.9		5_4-6_6
		3049.8	5_5-6_5
97	3049.7	3049.9	$4_{-4}-5_{-4}$
			2_0-3_0
96–*a*	3057.5	3057.4	$4_{-3}-5_{-5}$
96–*b*	3060.6	3061.3	$6_{-6}-6_{-4}$
			1_0-2_2
95	3065.2	3065.5	$3_{-3}-4_{-3}$
94	3067.7	3067.7	$5_{-4}-5_{-2}$
		3067.4	1_1-2_1
93–*a*	3077.6		?
93–*b*	3078.8	3079.2	$3_{-2}-4_{-4}$
92–*a*	3080.9	3080.5	$5_{-5}-5_{-3}$
		3080.8	$2_{-2}-3_{-2}$
92–*b*	3082.2	3082.3	$4_{-3}-4_1$
92–*c*	3083.9	3083.7	$4_{-1}-5_{-3}$
91	3086.9		?
90–*a*	3094.8	3094.8	$3_{-2}-3_0$
			6_6-7_6
90–*b*	3096.2	3096.2	6_5-7_7
			$6_{-1}-7_{-3}$
90–*c*	3096.9	3097.0	$1_{-1}-2_{-1}$
		3097.5	$5_{-5}-4_1$ W
		3100.2	$6_{-6}-5_0$
89	3100.9	3100.7	$4_{-1}-4_1$
		3101.2	$4_{-4}-4_{-2}$
88–*a*	3102.3	3102.3	$2_{-1}-3_{-3}$
88–*b*	3103.9	3104.1	3_0-3_2
		3104.2	$2_{-1}-2_1$
87–*a*	3105.6	3105.6	$6_{-4}-6_{-2}$
87–*b*	3108.2	3108.2	3_1-3_3
86–*a*	3115.0	3114.5	$5_{-1}-5_1$
		3115.2	0_0-1_0
86–*b*	3116.9	3116.9	$3_{-3}-3_{-1}$
		3117.2	5_1-5_3
85–*a*	3119.0	3119.1	4_1-4_3
85–*b*	3119.8	3119.7	4_2-4_4
		3120.1	2_0-2_2
84	3123.3	3123.2	$3_{-1}-3_1$
		3127.4	1_0-2_{-2}
83	3127.8	3127.5	6_0-6_2
		3127.9	$2_{-2}-2_0$
		3128.2	$5_{-3}-5_{-1}$
82–*a*	3132.6		
82–*b*	3134.1	3134.0	$1_{-1}-1_1$
82–*c*	3137.4		?
82–*d*	3141.3		?
82–*e*	3143.5	3143.3	6_1-6_3
82–*f*	3145.6	3146.6	2_1-3_{-1}
82–*g*	3149.7	3149.8	5_3-5_5
82–*h*	3158.2	3157.9	?
		3158.5	$6_{-5}-5_{-1}$
81–*a*	3166.5		?
81–*b*	3178.8	3178.4	1_1-1_{-1}
		3178.9	2_2-3_{-2}
80	3186.5	3186.1	$2_{-2}-2_0$
		3186.2	2_0-2_{-2}
		3197.2	$6_{-2}-7_{-6}$
79–*a*	3197.5	3197.4	1_0-0_0
		3197.5	6_4-6_6
		3197.7	6_3-6_5
			$4_{-1}-3_3$
79–*b*	3199.0	3198.6	$3_{-1}-3_{-3}$
		3210.8	$3_{-3}-2_{-1}$
76	3211.1	3210.9	4_0-3_2
		3211.4	3_3-4_{-1}
75	3215.3	3215.2	$2_{-1}-1_{-1}$
		3215.6	$4_{-2}-4_{-4}$
73–*a*	3220.7	3220.4	3_1-3_{-1}
		3221.0	4_0-4_{-2}
73–*b*	3223.5		?
72	3228.5	3228.5	$6_{-3}-5_1$
71–*a*	3230.8*	3231.2	$4_{-2}-3_0$
71–*b*	3231.1	3231.1	$3_{-2}-2_{-2}$
70	3234.2	3234.2	$4_{-4}-3_{-2}$
69–*a*	3237.8		?
	(0)	3239.4	5_1-4_3
69–*b*	3241.4	(?)3240.5	2_1-2_{-1}
		3240.9	$5_{-1}-4_1$
68	3246.0	3245.9	$4_{-3}-3_{-3}$
67	3249.4	3249.5	$5_{-3}-5_{-5}$
66	3255.1	3255.3	$5_{-5}-4_{-3}$
65	3258.2	3258.5	$4_{-1}-4_{-3}$
		3261.7	$6_{-4}-6_{-6}$
64	3261.6	3261.7	4_3-5_1
		3261.8	$5_{-4}-4_{-4}$
63	3266.3	3266.7	4_4-5_0
62	3274.9	3274.4	$5_{-3}-4_{-1}$
		3275.1	6_0-5_2
61	3277.5	3277.5	2_1-1_1
		3277.6	$6_{-6}-5_{-4}$
60–*a*	3279.7	3279.7	$6_{-2}-5_0$
		3279.8	$6_{-5}-5_{-5}$
60–*b*	3281.5	3281.1	5_1-5_{-1}
59–*a*	3284.1	3284.0	2_2-1_0
59–*b*	3285.5		?
58	3290.0	3290.2	$6_{-3}-6_{-5}$
		3290.0	6_1-5_5
57	3292.6	3292.2	4_2-4_0
		3292.4	$6_{-1}-7_{-7}$
			$6_{-4}-5_{-2}$
56	3294.2	3294.2	3_0-2_0
55	3299.0	3299.6	3_3-3_1
54–*a*	3304.1		?
54–*b*	3305.4	3305.2	3_2-3_0
53–*a*	3309.7	3309.9	$4_{-1}-3_{-1}$
53–*b*	3311.6	3311.3	6_3-7_1
53–*c*	3313.2		?
52	3314.3	3314.3	3_1-2_{-1}
		3314.8	6_4-7_0
51–*a*	3324.0		?
51–*b*	3325.9	3325.7	$6_{-1}-6_{-3}$
50–*a*	3329.7		?
50–*b*	3331.1		?
50–*c*	3332.7		?
49	3336.0		
48	3338.2	3337.9	$6_{-3}-5_{-3}$
		3338.2	5_5-6_1
47–*a*	3346.7		?
47–*b*	3348.4		?

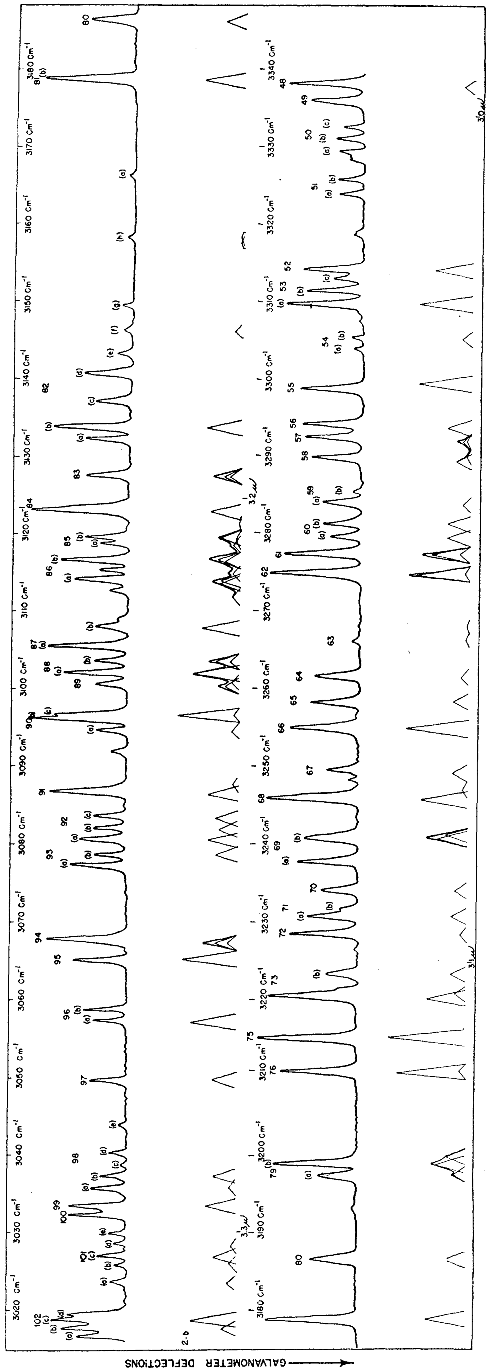

FIG. 2. Rotation vibration lines in the 3.3μ water vapor band.

by recording the absorptions due to the water vapor present in the optical path of the spectrometer itself. In the case of the less intense bands, it has apparently been impossible to operate the spectrometer with slits sufficiently narrow to give the desired definition and resolution.

It has been pointed out elsewhere[9] that it has been found practicable to surround the optical parts of the spectrometer in this laboratory with an airtight box so that the water vapor inside can be reduced to a mere fraction of the amount normally present. Under these conditions the lines can be almost completely resolved, a fact which seems to justify a complete remeasurement of the water vapor bands which lie in this region. These measurements, reported on earlier,[10] are now complete and in this paper, Part I, we wish to discuss our results on the fundamental band ν_2 and its overtone $2\nu_2$, both of which are due to oscillations of the electric moment parallel to the axis of the intermediate moment of inertia. Such oscillations are sometimes spoken of as perpendicular oscillations because they are perpendicular to both the axes of the largest and the smallest moments of inertia which in two different limiting cases may be thought of as approximate symmetry axes. We shall defer to Part II the discussion of our measurements on the bands originating with alternations of the electric moment parallel to the axis of the smallest moment of inertia.

II. EXPERIMENTAL

The spectrometer used to make these measurements is the same used in similar experiments carried out in this laboratory. As in the works by Sleator and his collaborators the water vapor in the optical path of the spectrometer itself was used as the absorbing layer. To obtain any resolution whatever of the lines in the fundamental band ν_2 which lies near 6.25μ, it was necessary to dry the air in the spectrometer thoroughly. This was accomplished by placing large glass trays containing P_2O_5 in the bottom of the box which surrounds the optical parts of the spectrometer. The box is made airtight by snapping into place the top of the box which is fashioned much like a refrigerator door. The instrument was allowed to stand from fifteen to

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[9] D. Cameron, W. C. Sears and H. H. Nielsen, J. Chem. Phys. **7**, 994 (1939).

[10] H. H. Nielsen, Phys. Rev. **55**, 346A (1940).

twenty hours for equilibrium to be reached inside before measurements actually were begun. One such charge of P_2O_5 was found sufficient to maintain the equilibrium for a week or more. In spite of these precautions there was still too much water vapor present, the peaks of the most intense lines causing absorption of nearly 100 percent.

For the measurements on the fundamental, an echellette grating ruled with 2000 lines per inch was used. The spectrometer could be operated successfully with slits equivalent to as little as 0.3 cm^{-1} and data were recorded at settings on the spectrometer circle separated by intervals equivalent to about 0.2 cm^{-1}. The data were recorded as galvanometer deflections. In order to obtain as accurate a representation as possible of the relative intensities of the lines throughout the band the foreprism of the instrument was set carefully beforehand so that the galvanometer deflections at settings between two absorption peaks were nearly the same at the beginning and at the end. The composite picture of the data obtained from many individual runs over the band is shown in Fig. 1(a) and the frequency positions of the lines, identified for convenience by the arbitrary numbers adopted by Plyler and Sleator, are given in the second column of Table I.

It was unnecessary to dry the air in the spectrometer to gather the data on the overtone band $2\nu_2$. The measurements were made with an echellette grating ruled with 4800 lines per inch. The spectrometer slits were narrowed so that they were equivalent to about 0.4 cm^{-1}. Galvanometer deflections were recorded at intervals on the circle equivalent to about 0.3 cm^{-1}. The composite absorption pattern of the band $2\nu_2$ is shown in Fig. 2(a) and in the second column of Table II the frequencies of the lines of the band will be found, identified again by the arbitrary numbers assigned to them by Plyler and Sleator.

In both of these curves, far better resolution of the lines has been achieved and much more detail has been observed. It is felt that until vacuum instruments are constructed for this region, little further improvement in the resolution of the water vapor bands can be hoped for.

III. IDENTIFICATION OF THE OBSERVED LINES

In this section we shall present our identification of the lines measured in the two bands ν_2 and $2\nu_2$ and from them deduce the positions of the vibration-rotation energy levels for these states. In this connection it is useful to review briefly some facts concerning the theory of the vibration-rotation spectra of such molecules and for our purpose we shall refer to the formulation of it presented by Shaffer and Nielsen.[11] In their notation the rotation energies for given values of the vibration quantum numbers V_1, V_2 and V_3 and the quantum number of total angular momentum J, are given by the relation:

$$E(V,J,\tau)=J(J+1)[\tfrac{1}{2}(A(V)+B(V))+\rho_1]-J^2(J+1)^2\rho_2+\epsilon_\tau, \tag{1}$$

where ϵ_τ is one of the $2J+1$ roots of the secular determinant containing the elements

$$\begin{aligned}(K|K)&=(R_2K^2+R_3K^4-\epsilon),\\(K|K\pm2)&=\{[f-K(K\pm1)][f-(K\pm1)(K\pm2)]\}^{\frac{1}{2}}\{R_4+R_5[K^2+(K\pm2)^2]\},\\(K|K\pm4)&=\{[f-K(K\pm1)][f-(K\pm1)(K\pm2)][f-(K\pm2)(K\pm3)][f-(K\pm3)(K\pm4)]\}^{\frac{1}{2}}R_6,\end{aligned} \tag{2}$$

in which $R_2=[C(V)-\frac{1}{2}(A(V)+B(V))-5\rho_1/2]+J(J+1)\rho_3$ and

$$R_4=[\tfrac{1}{4}(A(V)-B(V))-J(J+1)\rho_4],$$

$A(V)$, $B(V)$ and $C(V)$ being respectively $\dot{h}/8\pi^2c$ times the reciprocals of the moments of inertia

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[11] In this paper the following typographical errors have been detected: (1) the sign preceding the third term in Eq. (35) should be negative; (2) in the last term of the equation defining Y_0, the sign preceding the coefficient of $\cos\gamma/\omega_2{}^2$ should be negative; (3) in the second line of the definition of Z_0, $\hbar/C_0{}^2$ should be replaced by $\hbar/C_0$; (4) in the equation defining Y_1 the ω_2 outside the braces should be ω_1 and the sign before the second term should be $+$; (5) in the equation defining Y_2 the sign before the second term inside the braces should be $-$; (6) the subscripts associated with the quantities R_i in (41) and (42) should run from $i=1$ to $i=6$ and not from $i=0$ to $i=5$; (7) in the definition of k_1' in relations (10) the quantity $(K_4/2)$ should be replaced, by $(K_4/4)$; (8) in the definition of k_3' in (10) $\cos^2\alpha$ should be replaced by $\sin^2\alpha$.

$(I_x^{(e)})$, $(I_y^{(e)})$ and $(I_z^{(e)})$[12] effective in the given vibration state. The quantities ρ_1 and R_3, R_5 and R_6 which occur in (1) and (2) are coefficients of the centrifugal distortion of the molecule. They are in general complicated expressions depending upon the normal frequencies and the size and shape of the molecule and their definitions may be obtained by reference to the work by Shaffer and Nielsen. The symbol f is introduced for $J(J+1)$.

The effective reciprocals of inertia depend in a linear manner upon the vibration quantum number

$$A(V)=\frac{h}{8\pi^2c}\{1/I^0{}_x+\sum_{V\,i=1}^{3}(V_i+\tfrac{1}{2})X_i\}=\frac{h}{8\pi^2cI_x^{(e)}},$$

$$B(V)=\frac{h}{8\pi^2c}\{1/I^0{}_y+\sum_{V\,i=1}^{3}(V_i+\tfrac{1}{2})Y_i\}=\frac{h}{8\pi^2cI_y^{(e)}},\quad(3)$$

$$C(V)=\frac{h}{8\pi^2c}\{1/I^0{}_z+\sum_{V\,i=1}^{3}(V_i+\tfrac{1}{2})Z_i\}=\frac{h}{8\pi^2cI_z^{(e)}},$$

where the X_iY_i and Z_i are quantities depending in an involved way upon the potential energy constants. The moments of inertia themselves obey a law similar to that for $A(V)$, $B(V)$ and $C(V)$ and to this approximation they are also linear in V_i. Concerning these Darling and Dennison have pointed out that there exists a relation[13]

$$I_z^{(e)}-I_x^{(e)}-I_y^{(e)}=\Delta,\quad(4)$$

where Δ is independent of the anharmonic potential energy constants and may therefore be calculated from a knowledge only of the normal frequencies and the size and shape of the molecule.

The theoretical evaluation of the roots ϵ_τ is done by expanding the secular determinant whose elements are given in (2). This expansion is considerably more complicated than that of the ordinary asymmetrical top secular determinant[14] due to the extra $(K|K\pm4)$ elements arising from the inclusion of centrifugal stretching terms in the energy expression. The actual expansion of the determinant is facilitated by the method suggested in the paper by Shaffer and Nielsen. Since the elements are diagonal in J and M, the determinant factors into steps in each of which J and M are constant; the nondependence of the elements (2) on M shows that the steps are identical for all the possible $2J+1$ values of M associated with a given J, hence only one step needs to be expanded for each J value. Each of the J steps can be factored into two substeps, one associated with even and the other with odd values of K; thus for each J there is a substep of order J and one of order $J+1$. It is interesting to note that when expressed in terms of the R_i, the $(J+1)$th order step associated with a given J is formally identical with the J'th order substep associated with $J'=J+1$; this fact reduces considerably the work required to evaluate the roots ϵ_τ since only one of the substeps associated with a given J needs to be expanded because the other one has been expanded already for the preceding value of J. The substeps can be further factored by taking plus and minus linear combinations of the rows and columns associated with a given K. For our purpose it has been useful to expand the determinant for all values of J up through $J=6$, and the algebraic relations for the ϵ_τ are given below. For each value of J only the equations arising from the substep of order $J+1$ are given, those due to the substep of order J being identical with the one occurring for the preceding J value:

$J=0 \quad \epsilon=0$

$J=1 \quad \epsilon=(R_2+R_3)\pm(R_4+2R_5)f,$

$J=2 \quad \epsilon=[4R_2+16R_3-R_6f(f-2)],$

$\epsilon=\tfrac{1}{2}[4R_2+16R_3+R_6f(f-2)]\pm\tfrac{1}{2}\{[4R_2+16R_3+R_6f(f-2)]^2+8f(f-2)(R_4+4R_5)^2\}^{\frac{1}{2}},$

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[12] To conform with a notation used by many molecular spectroscopists $A(V)$, $B(V)$ and $C(V)$ has been chosen to represent $h/8\pi^2c$ times the reciprocals of the effective moments of inertia. In the notation of Shaffer and Nielsen the effective moments of inertia are A_e, B_e and C_e. To avoid confusion we have replaced this notation respectively by $I_x^{(e)}$, $I_y^{(e)}$ and $I_z^{(e)}$.

[13] This relation may be verified by using for $I_x^{(e)}$, $I_y^{(e)}$ and $I_z^{(e)}$ the quantities $A(V)$, $B(V)$ and $C(V)$ expanded to the power -1, retaining only that term linear in $(V_i+\frac{1}{2})$.

[14] S. C. Wang, Phys. Rev. **34**, 243 (1929).

$$\begin{aligned}
J=3\quad & \epsilon=\tfrac{1}{2}[10R_2+82R_3\mp(R_4+2R_5)f]\pm\tfrac{1}{2}\{[8R_2+80R_3\pm(R_4+2R_5)f]^2\\
&\qquad\qquad +4(f-2)(f-6)(R_4+10R_5\mp fR_6)^2\}^{\frac{1}{2}},\\
J=4\quad & \epsilon=\tfrac{1}{2}[20R_2+272R_3-f(f-2)R_6]\pm\tfrac{1}{2}\{[12R_2+240R_3+f(f-2)R_6]^2\\
&\qquad\qquad +4(f-6)(f-12)(R_4+20R_5)^2\}^{\frac{1}{2}},\\
\text{roots of }\; & \epsilon^3-[20R_2+272R_3+f(f-2)R_6]\epsilon^2+[64(R_2+16R_3)(R_2+4R_3+f(f-2)R_6/4)\\
& -(f-6)(f-12)(R_4+20R_5)^2-2f(f-2)(R_4+4R_5)^2-2f(f-2)(f-6)(f-12)R_6{}^2]\epsilon\\
& +32f(f-2)(R_2+16R_3)(R_4+4R_5)^2+[8(R_2+4R_3+f(f-2)R_6/4)R_6{}^2\\
&\qquad\qquad -4(R_4+4R_5)(R_4+20R_5)R_6]f(f-2)(f-6)(f-12)=0\\
J=5\quad & \epsilon^3-[35R_2+707R_3\mp(R_4+2R_5)f]\epsilon^2+[225(R_2+9R_3)(R_2+35R_3)\\
& +(34R_2+706R_3)(R_2+R_3\mp(R_4+2R_5))-(f-12)(f-20)(R_4+34R_5)^2\\
& -(f-2)(f-6)(R_4+10R_5\pm fR_6)^2-(f-2)(f-6)(f-12)(f-20)R_6{}^2]\epsilon\\
& -[225(R_2+9R_3)(R_2+25R_3)(R_2+R_3\mp(R_4+2R_5)f)-25(f-2)(f-6)(R_2+25R_3)\\
& \times(R_4+10R_5\pm fR_6)^2-(f-12)(f-20)(R_4+34R_5)^2(R_2+R_3\mp(R_4+2R_5)f)\\
& +(f-2)(f-6)(f-12)(f-20)(2(R_4+34R_5)(R_4+10R_5\pm fR_6)R_6-9(R_2+9R_3)R_6{}^2)]=0,\\
J=6\quad & \epsilon^3-[56R_2+1568R_3-f(f-2)R_6]\epsilon^2+[576(R_2+16R_3)(R_2+36R_3)\\
& +4(13R_2+388R_3)(4R_2+16R_3-f(f-2)R_6)-(f-6)(f-12)(R_4+20R_5)^2\\
& -(f-20)(f-30)(R_4+52R_5)^2-(f-6)(f-12)(f-20)(f-30)R_6{}^2]\epsilon\\
& -[576(R_2+16R_3)(R_2+36R_3)(4R_2+16R_3-f(f-2)R_6)-36(f-6)(f-12)\\
& \times(R_2+36R_3)(R_4+20R_5)^2-(f-20)(f-30)(R_4+52R_5)^2(4R_2+16R_3-f(f-2)R_6)\\
& +2(f-6)(f-12)(f-20)(f-30)R_6(R_4+20R_5)(R_4+52R_5)\\
&\qquad\qquad -16(f-6)(f-12)(f-20)(f-30)(R_2+16R_3)R_6{}^2]=0,\\
& \epsilon^4-[56R_2+1568R_3+f(f-2)R_6]\epsilon^3+[576(R_2+16R_3)(R_2+36R_3)+4(13R_2+388R_3)\\
& \times(4R_2+16R_3+f(f-2)R_6)-(f-6)(f-12)(R_4+20R_5)^2-(f-20)(f-30)(R_4+52R_5)^2\\
& -(f-6)(f-12)(f-20)(f-30)R_6{}^2-2f(f-2)((R_4+4R_5)^2+(f-6)(f-12)R_6{}^2)]\epsilon^2\\
& -\{576(R_2+16R_3)(R_2+36R_3)(4R_2+16R_3+f(f-2)R_6)-36(f-6)(f-12)\\
& \times(R_2+36R_3)(R_4+20R_5)^2-(f-20)(f-30)(R_4+52R_5)^2(4R_2+16R_3+f(f-2)R_6)\\
& +2(f-6)(f-12)(f-20)(f-30)(R_4+20R_5)(R_4+52R_5)R_6-16(f-6)(f-12)\\
& \times(f-20)(f-30)(R_2+16R_3)R_6{}^2+4f(f-2)(f-6)(f-12)(R_4+4R_5)(R_4+20R_5)R_6\\
& -2f(f-2)(f-6)(f-12)R_6{}^2(40R_2+1312R_3+f(f-2)R_6)\\
& -8f(f-2)(R_4+4R_5)^2(13R_2+388R_3)\}\epsilon-1152f(f-2)(R_4+4R_5)^2(R_2+16R_3)\\
& \times(R_2+36R_3)+2(R_4+4R_5)^2(R_4+52R_5)^2f(f-2)(f-20)(f-30)-4f(f-2)(f-6)\\
& \times(f-12)(f-20)(f-30)(R_4+4R_5)(R_4+52R_5)R_6{}^2+144f(f-2)(f-6)(f-12)\\
& \times(R_4+4R_5)(R_4+20R_5)(R_2+36R_3)R_6-72(R_2+36R_3)(4R_2+16R_3+f(f-2)R_6)R_6{}^2\\
& \times f(f-2)(f-6)(f-12)+2R_6{}^4f(f-2)(f-6)^2(f-12)^2(f-20)(f-30)=0.
\end{aligned}\tag{5}$$

When the centrifugal distortion coefficients ρ_i, R_3, R_5 and R_6 have been computed and inserted into Eqs. (1) and (5) inspection will show that it is possible to evaluate the moments of inertia effective in a given vibration state if it is possible to identify enough lines in the band so as to determine the rotational energies for $J=1$ and $J=2$. In principle then these constants can be inserted into the above equations and used to compute the energies for higher values of J. This should then facilitate the further identification of other lines in the spectrum. When this is tried on the energies given by Randall, Dennison, Ginsburg and Weber (RDGW) for the molecule in the normal state it is found, however, that the energies for higher J values computed in this manner are not in extremely good agreement with the values found experimentally. The explanation for this is given by RDGW who point out that the centrifugal distortion is not adequately taken into account by the terms quartic in the rotational quantum numbers, but that these represent them only in first approximation.

We have, therefore, proceeded in a somewhat different manner. We have assumed that the rotation energies in the state $V_1=V_2=V_3=0$ are known more accurately than those for any other vibration state. We have equated the experimental values of the energies to the corresponding theoretical energies up through $J=5$, using only those, however, where ϵ can be expressed explicitly. In this manner we have solved for the values of the effective moments of inertia and the centrifugal stretching coefficients which reproduce the experimental data as a whole most faithfully. These quantities will, in general, not satisfy the relations which the theory demands and no real physical significance can be attached to them. Their only justification is that they reproduce the experimental data quite faithfully over a large range of J values and are therefore useful in extrapolating to considerable accuracy the energies for still higher values of J. It is found, however, that the moments of inertia effective for the normal vibration state determined in this manner have only a small percent deviation from those determined by Darling and Dennison by the more rigorous method. The percent deviation between the centrifugal stretching coefficients, which are all small, determined by this method and those calculated are often large. They are, nevertheless, always of the same order of magnitude and have the right algebraic signs. For the sake of comparison we insert Table III which gives the calculated and observed values of the coefficients of centrifugal distortion. Since these coefficients are independent of the vibration quantum numbers, we shall assume that the values determined from the data for the normal state are also valid for the states ν_2 and $2\nu_2$.

TABLE III. *Observed and calculated values of* ρ_i, R_3, R_5 *and* R_6.

	OBSERVED VALUE	CALCULATED VALUE
ρ_1	1.497×10^{-2}	1.0495×10^{-2}
ρ_2	4.73×10^{-2}	1.503×10^{-2}
ρ_4	4.5×10^{-3}	4.871×10^{-3}
R_3	-3.028×10^{-2}	-5.699×10^{-3}
R_5	9.5×10^{-3}	1.67×10^{-3}
R_6	-6.6×10^{-4}	-6.75×10^{-4}

The fundamental band ν_2

Each line in this band is due to the molecules making a transition from a rotation level in the normal vibration state to a rotation level in the state ν_2 and its frequency will be the difference between a term value in ν_2 and one in the normal state. The frequency ν_2 is due to an oscillating electric moment parallel to the axis of the intermediate moment of inertia. The selection rules for this case have been conveniently formulated by Dennison[15] and need not be restated here. By trial and error enough lines are identified so that the term values for the quantum numbers $J=0$, $J=1$ and $J=2$ can be established. As a check that the identifications are right, combination relations are employed. For example, we have identified the following lines $1_0-2_{-2}=1565.1$, $1_0-2_2=1499.1$ and $1_0-0_0=1635.2$. Using for the term values in the normal state those given by RDGW we obtain for the rotation level 1_0 in cm^{-1} the values 1635.1, 1635.2 and 1635.2, all of which are in good agreement. By identifying the experimentally determined term values for $J=0$, $J=1$ and $J=2$ with the corresponding of the Eq. (1),

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[15] D. M. Dennison, Rev. Mod. Phys. **3**, 280–345 (1931).

TABLE IV. *Rotation-vibration energies for the states ν_2 and $2\nu_2$ in the water vapor molecule.*

	Energies in cm^{-1} for State			Energies in cm^{-1} State			Energies in cm^{-1} State	
J_τ	ν_2	$2\nu_2$	J_τ	ν_2	$2\nu_2$	J_τ	ν_2	$2\nu_2$
0_0	1595.4	3152.3	4_4	2132.2	3770.6	5_{-3}	2000.8	3574.7
			4_3	2132.2	3770.6	5_{-4}	1922.4	3483.7
1_1	1641.2	3202.2	4_2	2006.6	3607.9	5_{-5}	1920.7	3480.0
1_0	1635.3	3197.4	4_1	2005.2	3607.3			
1_{-1}	1618.6	3176.4	4_0	1923.4	3496.2	6_6	2750.8	4491.5
			4_{-1}	1908.1	3483.2	6_5	2750.8	4491.5
2_2	1743.8	3321.1	4_{-2}	1875.3	3437.5	6_4	2560.1	4242.8
2_1	1742.5	3319.9	4_{-3}	1821.3	3382.6	6_3	2560.1	4242.8
2_0	1694.2	3256.2	4_{-4}	1817.6	3376.4	6_2	2401.8	
2_{-1}	1677.1	3239.0				6_1	2401.0	4032.3
2_{-2}	1665.4	3223.0	5_5	2412.3	4095.1	6_0	2289.1	3885.3
			5_4	2412.3	4095.1	6_{-1}	2270.6	3878.7
3_3	1908.1	3511.7	5_3	2254.9	3892.1	6_{-2}	2211.5	3783.7
3_2	1908.0	3511.5	5_2	2253.6	3891.2	6_{-3}	2161.9	3737.4
3_1	1819.5	3393.7	5_1	2130.4	3727.6	6_{-4}	2137.9	3708.4
3_0	1814.1	3389.4	5_0	2126.7		6_{-5}	2043.0	3605.0
3_{-1}	1772.6	3335.3	5_{-1}	2052.4	3623.4	6_{-6}	2043.0	3604.1
3_{-2}	1739.7	3301.1	5_{-2}	2024.2				
3_{-3}	1732.2	3290.2						

using for the coefficients of centrifugal stretching those determined above we may obtain new values for R_1, R_2 and R_4 which will be effective for this state. With the values of $R_1(\nu_2)$, $R_2(\nu_2)$ and $R_4(\nu_2)$ so determined it is possible to compute the values of the rotational energies for higher values of J and from these predict where additional lines are to be expected in the spectrum. Once these new lines have been identified definitely we may make use of them to improve upon the values of $R_i(\nu_2)$ and then proceed to identify additional lines. It was found that this method was extremely useful in identifying the lines in the band ν_2. To insure that the energy levels were correctly assigned, combination relations similar to those referred to above have been used consistently and in all cases the agreement has been gratifyingly good. Lines in the spectrum originating from transitions between levels up to and including $J=6$ have been identified and it is found that nearly all the important lines on either side of the center of the band to a distance of about 100 cm^{-1} have been accounted for. The identifications of the lines in the band ν_2 are given in the fourth column of Table I. The values of the rotation-vibration energies for the state ν_2 as deduced from these identifications are given in the first column of Table IV for the quantum numbers J up through $J=6$. From these the positions of the lines have been recomputed and for the sake of comparison are given in the third column of Table I.

As a further verification that the identifications of the lines in the band are correct, their intensities have been computed and compared with those observed. The calculation of the intensities is simple in principle, but for a molecule like water vapor, it becomes a complicated procedure in practice. This is because the molecule is an asymmetric top for which the eigenfunctions $\chi(J, \tau, M)$, which are necessary to compute the matrix components of the electric moment, are linear combinations of the wave functions $\Psi(J, K, M)$ for a symmetric top. These may be written:

$$\chi(J, \tau, M)=\sum C_{J,\tau,M}\Psi(J, K, M), \qquad (6)$$

where the coefficients $C_{J,\tau,M}$ are the normalized subminors of the secular determinant $|(K|H|K')-E\delta_{KK'}|$. The evaluation of the coefficients $C_{J,\tau,M}$ is very laborious and to be at all rigorous it would be necessary to evaluate them not only for the state ν_2, but for the normal state as well, since the effective moments of inertia, and therefore also the effective asymmetry of the molecule, are different in the two states. This was actually done for the lowest transitions, but for the remaining transitions the approximation method discussed by RDGW has been employed. How satisfactory this method is may be subject to some discussion, but it is found that in general the intensities computed in this manner agree well with those observed. Actual quantitative agreement could hardly be hoped for under any circumstances since even after drying the air the most intense lines represent nearly 100 percent absorption and are still quite broad. In order to make an actual comparison with the observed spectrum, we have plotted a spectrum as predicted theoretically using as term values those given by RDGW for the normal state and those in Table IV for the state ν_2. Each line is drawn as a triangle the base of which is roughly twice that of the spectrometer slit and the altitude of which is proportional to the calculated intensity. In certain cases the lines lie very close together in groups. In such cases a more satisfactory comparison is made by drawing in the composite envelope of the components. This band is shown in Fig. 1(b), below the curve observed experimentally. We feel that the

TABLE V. *Theoretical and observed values of* $I_x^{(e)}$, $I_y^{(e)}$, $I_z^{(e)}$ *and* Δ.

(V_1, V_2, V_3)	$I_x^{(e)}$ (OBS.)	$I_x^{(e)}$ (CALC.)	$I_y^{(e)}$ (OBS.)	$I_y^{(e)}$ (CALC.)	$I_z^{(e)}$ (OBS.)	$I_z^{(e)}$ (CALC.)	Δ (OBS.)	Δ (CALC.)
(0, 1, 0)	0.905	0.906	1.902	1.907	3.054	3.055	0.247	0.241
(0, 2, 0)	0.775	0.805	1.895	1.892	3.095	3.092	0.425	0.411

agreement between the two is extremely satisfactory. A few lines remain which have not been identified, but in no case has a line of considerable intensity been predicted where none is observed. It seems reasonable to ascribe the lines which remain unidentified as due to transitions between levels of still higher J values.

The overtone band $2\nu_2$

The overtone band is due also to an oscillating electric moment parallel to the axis of the intermediate moment of inertia and the selection rules are therefore entirely the same as before. Our procedure in this case has therefore been entirely the same as before. By trial and error, enough lines were identified to obtain temporary values for the $R_i(2\nu_2)$. With these, lines in the spectrum were predicted and in most cases these were found to be sufficiently close to experimentally measured lines to aid materially in the analysis. Again the identifications were verified by using combination relations. The identifications assigned to the lines in $2\nu_2$ are given in the fourth column of Table II and from these the rotation levels for this state have been deduced up through $J=6$. These are given in the third column of Table IV. Again the positions of the lines in the band have been recomputed from the term values and are set down for comparison in the third column of Table II. A theoretical spectrum has also here been plotted for comparison with the experimental curve and will be found in Fig. 2(b). In general, the agreement is quite satisfactory. More lines remain unidentified in this case than in ν_2, but most of these can, no doubt, be attributed to transitions between energies of higher J values. Because of the nearness of $2\nu_2$ to the fundamental ν_3, it does not seem entirely impossible that some of the lines remaining unidentified are lines belonging to that band.

IV. EVALUATION OF THE CONSTANTS OF THE MOLECULE

It is now possible on the basis of what has gone before to calculate certain new constants of the molecule and verify the values of others already computed by Darling and Dennison. We shall first consider the constants occurring in the vibration energy. This may be written

$$E(V_1V_2V_3)/hc = E_0/hc + \sum_{i=1}^{3} (V_i+\tfrac{1}{2})\nu_i + \sum_{i\geq k} (V_i+\tfrac{1}{2})(V_k+\tfrac{1}{2})U_{ik}, \quad (7)$$

where ν_i are the normal frequencies and the U_{ik} are relations depending in an involved manner on the potential energy constants. Their definitions for the rotating-vibrating molecule have been given by Shaffer and Nielsen, and as far as the potential energy is concerned are entirely equivalent to the definitions in the earlier work by Bonner (in his notation X_{ik}). The two bands ν_2 and $2\nu_2$ arise when the molecule executes a vibrational transition from the normal state where $V_1=V_2=V_3=0$ to the states where $V_2=1$, $V_1=V_3=0$ and where $V_2=2$, $V_1=V_3=0$, respectively, their frequencies being given by the Bohr frequency condition. For the first of these we obtain $\nu'=\nu_2+2U_{22}$ and for the second we have $\nu''=2\nu_2+6U_{22}$. The vibration energies are in each case coincident with the rotation-vibration state 0_0 so that we have $\nu_2+2U_{22}=1595.4$ cm^{-1} and $2\nu_2+6U_{22}=3152.3$ cm^{-1}. These lead at once to the value $U_{22}=-19.25$ cm^{-1}, in good agreement with that given by Darling and Dennison. Taking as the values for the other U_{ik} those given by them we obtain for the normal frequency the value $\nu_2=1653.8$ cm^{-1}.

From their study of the vibration-rotation data of the water vapor molecule Darling and Dennison have arrived at the following numerical relations as most representative of the correct values for the effective moments of inertia:

$$\begin{aligned} I_x^{(e)}\times 10^{40} &= 1.0229+(0.0213)(V_1+\tfrac{1}{2}) \\ &\quad -(0.1010)(V_2+\tfrac{1}{2})+(0.0486)(V_3+\tfrac{1}{2}), \\ I_y^{(e)}\times 10^{40} &= 1.9207+(0.0398)(V_1+\tfrac{1}{2}) \\ &\quad -(0.0249)(V_2+\tfrac{1}{2})+(0.0077)(V_3+\tfrac{1}{2}), \quad (8) \\ I_z^{(e)}\times 10^{40} &= 2.9436+(0.0611)(V_1+\tfrac{1}{2}) \\ &\quad +(0.0385)(V_2+\tfrac{1}{2})+(0.0441)(V_3+\tfrac{1}{2}). \end{aligned}$$

It is of interest to compute from the above data what are the values of the moments of inertia $I_x^{(e)}$, $I_y^{(e)}$ and $I_z^{(e)}$ effective in the states ν_2 and $2\nu_2$ for comparison with the values predicted by the relations (8). To do this we have confined ourselves to the use of the rotation-vibration energies up through $J=3$ since in these states the centrifugal distortion is small so that the energy relations (1) may be regarded as fairly rigorous. The values $\frac{1}{2}(1/I_x^{(e)}+1/I_y^{(e)})$, $-\frac{1}{2}(1/I_x^{(e)}+1/I_y^{(e)})+1/I_z^{(e)}$ and $\frac{1}{4}(1/I_x^{(e)}-1/I_y^{(e)})$ were averaged over these states, a little more weight being given to the values for which $J=2$ and $J=3$ since the constants will there be less affected by the inaccuracies of measurement. The coefficients of centrifugal distortion which were used were those calculated on a purely theoretical basis. The results of this calculation are to be found in Table V.

It will be seen that the agreement between the calculated and observed values of the moments of inertia effective for ν_2 and $2\nu_2$ as well as for Δ is consistently better than that arrived at by Darling and Dennison on the basis of the earlier data available to them on these bands. The improved values for the fundamental band and the new ones deduced from our analysis of the overtone band $2\nu_2$ represent a satisfactory bit of verification of the theory of the water vapor molecule.

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Electron Emission of Metals in Electric Fields

I. Explanation of the Periodic Deviations from the Schottky Line

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The periodic deviations from the Schottky line observed by Phipps and his collaborators and by Nottingham in measuring the thermionic emission of electrons from tungsten and tantalum can be interpreted as being due to the partial reflections of the electron waves on the potential hill at the surface of the metal. These partial reflections give rise to interference and thus to a periodic term in the transmission coefficient for the escaping electrons. The transmission coefficient is obtained by using the functions of the parabolic cylinder to establish the connection between the asymptotic expansions of the wave functions to the left and right of the top of the potential hill. The calculated positions of the maxima and minima of the deviations agree very well with the observed positions. In agreement with experiment, it is found that the positions of the maxima and minima are sensibly independent of temperature; and the amplitude decreases as the temperature is increased. The calculated amplitude of the deviations increases with the field, as does the observed amplitude. A dependence upon the work function of the emitting metal is obtained; however, since the heights of the surface potential barriers of tungsten and tantalum are very nearly equal, no experimental data on this dependence are available.

I. Introduction

When electrons are emitted from a metal by the application of heat, or of an electric field, or of both simultaneously, one has the following expression for the emitted electron current

$$i=\int_0^\infty N(W)D(W,F)dW, \qquad (1)$$

where $N(W)$ is the number of electrons with energy W normal to the emitting surface. $N(W)$ is given by the Fermi distribution in the energy, which holds for the electrons in the metal; and $D(W, F)$ is the transmission coefficient for the electrons incident on the potential barrier at the metal surface with energy W normal to the surface. The potential field which the emitted