produce the "bay"-type magnetic disturbance which frequently occurs during magnetic storms are shown in Fig. 6.[12] While the currents necessary to produce the solar-flare disturbance are greatest close to the subsolar point and do not flow beyond the twilight zone, those necessary to produce the bay-type disturbance are much more pronounced near the auroral zone (about 70° north) and extend over the entire earth. The form of the apparent system of circulation is obviously different in both cases.

Actual records of the sudden commencement of a magnetic storm at various observatories are shown in Fig. 7. This represents another type of magnetic disturbance quite different from the other two, but one which is characteristic of the beginning of a magnetic storm. The outstanding characteristic of this disturbance is its widespread manifestation, in sharp contrast to the circumscribed manifestation of a solar-flare disturbance. Obviously, the mechanism which gives rise to the sudden commencement of a magnetic storm must be quite different from that which operates when a sudden flare of ultraviolet light from the sun impinges on the earth's atmosphere.

Acknowledgment.—The writer expresses his appreciation to various individuals and organizations which have made available to him the special data necessary for this study, and in particular to Dr. J. A. Fleming, Director of Carnegie Institution's Department of Terrestrial Magnetism, whose recognition of the importance of these phenomena has caused him to encourage and support the investigation of which this is a part.

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[12] A. G. McNish, Trans. Am. Geophys. Union, 17th annual meeting, 166 (1936).

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The Far Infrared Spectrum of Water Vapor

H. M. Randall, D. M. Dennison, Nathan Ginsburg and Louis R. Weber
University of Michigan, Ann Arbor, Michigan

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The rotation spectrum of water vapor has been measured with high dispersion from 18μ to 75μ. The spectrometer employed echelette gratings and higher spectral orders were successfully removed through the use of filters and selective reflection. The positions of single lines were determined with an accuracy of about 0.05 cm^{-1} throughout the entire region while neighboring lines as close together as 0.5 cm^{-1} could be separated and measured. The analysis of the spectrum was accomplished in the following manner. From the values of the moments of inertia found by Mecke the energy levels were calculated from the asymmetric rotator equations. However, these computed levels are often far from the actual energy levels due to the presence of a large correction arising out of the centrifugal force stretching of the molecule. An estimate of this correction, which amounted in some cases to over 200 cm^{-1}, was made, thus furnishing energy levels with which to begin the analysis. The intensities of the rotation lines were calculated by using as an approximation the symmetric rotator amplitudes. By comparing the expected spectrum with the observed spectrum it was then possible to identify the lines and through them to determine the actual energy levels of the water vapor molecule. Combination relations as well as the formation of analytic series from analogous lines, served as important checks on the identifications. Through these methods the rotational energy levels of the water molecule have been found up to and including the group of $J=11$ with an accuracy around 0.1 cm^{-1}. The highest level determined, possesses an energy of over 3200 cm^{-1}, while all the rotational levels with energies less than 2000 cm^{-1} have been obtained. Finally all the allowed transitions together with their intensities are calculated and these are plotted directly above the observed spectrum. The agreement is remarkably good. All the essential features of the spectrum and indeed most of the finer details are correctly reproduced.

I. Experimental

The present investigation covers the spectral region extending from 18μ to 75μ, thus overlapping somewhat the work of Wright and Randall[1] which began at 60μ. This earlier work demonstrated that the equipment used was capable of resolving and measuring the rotation spectrum of water with a completeness and accuracy not hitherto attained in this region of the spectrum. It was, however, so responsive to outside disturbances that much time was lost waiting for favorable conditions, often to be

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[1] Norman Wright and H. M. Randall, Phys. Rev. **44**, 39 (1933).

obtained at night only. The spectrograph employed was the one designed by Randall[2] and following this first investigation he was able to find means of overcoming this defect of unsteadiness so that observations are now generally possible at any time during the day: only very seldom are outside disturbances of sufficient magnitude as to interrupt work. In Fig. 1 the first set of data taken in this investigation is shown. The grating was turned by steps of 1 minute of arc and a *single* galvanometer deflection only was taken for each position. The definiteness with which each line is determined clearly indicates the steadiness of the instrument. The seven lines lie between 22.5 and 23.6μ, covering a frequency range of 20 cm^{-1}. This very complete freedom from chance effects has permitted an amplification of from 150 to 300 times, which is somewhat greater than was previously used. This makes narrower slits possible with a corresponding increase in resolution. The measurable limit of 1 cm^{-1} between the lines of a narrow doublet established in the investigation of Wright and Randall is now reduced to 0.5 cm^{-1}.

By using essentially the same technique as in the earlier work the accuracy now attained in measuring sharp lines which are free from overlapping by adjacent lines is about 0.003μ in the shorter wave-length region, with less accuracy as 70μ is approached. The accuracy in terms of waves per cm appears to be about 0.05 cm^{-1} throughout the spectrum measured. The slit width of 0.5 mm at the center of the region measured with the 1200 line grating, namely at about 23μ, covered a spectral range of approximately 0.005μ. At 34μ, using the 900 line grating, the slit was 1 mm wide and corresponded to a spectral aperture of 0.01μ. Between 40 and 75μ the slits were 1.5 mm wide which with the 360 line grating meant a spectral range of 0.05μ. Under these circumstances, lines 1.5 cm^{-1} apart are completely resolved, while those but 0.5 cm^{-1} apart are clearly double and quite accurately measurable.

The 1200 line grating, having a ruled surface of 9×9 inches, was designed to locate the blaze or region of maximum energy at 18μ. The 900 line grating, surface 10×20 inches, had its blaze at 23.4μ while the blaze of the 360 line grating, surface 10×20 inches, was located at 57μ. In general it is advisable to work to one side or the other of the blaze, as the radiation of short wave-length concentrated at this place is so great that the devices adopted, to purify the spectrum elsewhere, are not always effective here. The methods of calibration were those described in the first paper.

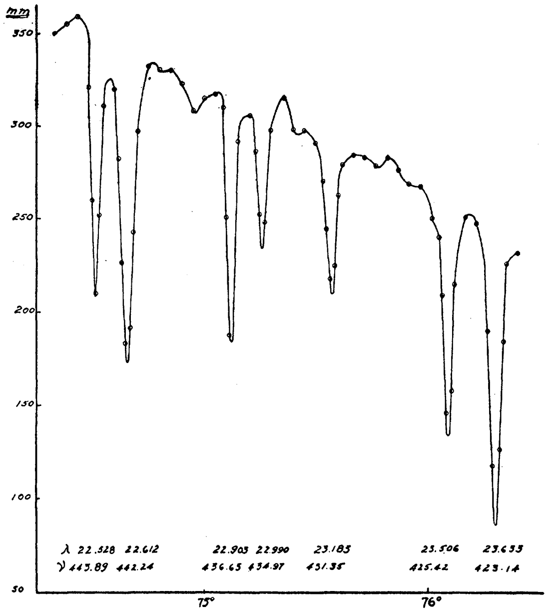

FIG. 1. The rotation spectrum of water.

Echelette gratings may be ruled to conserve the radiation in any spectral region but the desired first-order spectrum is overlaid with higher orders of radiation of shorter wave-length. These higher orders are removed in large part by absorbing screens and by selective reflections. The remaining energy of the higher orders is neutralized by employing shutters transparent to them but opaque to the longer wave-length radiation. Since this procedure is generally wasteful of the desired first-order spectra, the relatively large quantity of energy made available by this spectrometer through its large aperture and gratings permits not only greater dispersion but also greater losses in order to obtain the required degree of purity of spectrum. In the region between 18 and 30μ, a paraffin filter 1 mm thick, selective reflection from fluorite and a shutter of rocksalt cut out all

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[2] H. M. Randall, Rev. Sci. Inst. 3, 196 (1932).

observable effects of higher orders. Moreover the absorption of water vapor in the region between 9 and 15μ is so slight that second-order lines of measurable intensity are not likely to occur. To work between 25 and 40μ the only change necessary is that the selective reflection from a plate of sodium fluorite replaced that from fluorite. From 40 to 70μ, filters of paraffin and of crystal quartz each 1 mm thick together with shutters, first of potassium chloride, and then of potassium bromide, gave very satisfactory results. With a spectrum so rich in lines it is inevitable that the higher orders of some of the shorter wave-length lines will have values which will be in close agreement with the measured values of first order lines of longer wave-length. A careful study has been made of all such cases and it is believed that the results given have not been measurably affected by such possible overlappings.

This investigation was begun in April, 1934, and continued through the early summer. A sabbatical leave interrupted the work and in the meantime, June 15, 1935, a paper in this same field by Barnes, Benedict and Lewis[3] was published. From this paper it seemed quite probable that the higher resolution given by the spectrograph here used would be necessary if a successful interpretation of the rotation spectrum of water vapor in the far infrared was to be made. The work was accordingly continued.

II. ANALYSIS OF THE WATER SPECTRUM

In the remaining portion of this paper we shall attempt to identify the lines which have been found experimentally and thereby to determine the rotational energy levels of the water molecule. The measurements obtained in the present investigation will be combined with results found by Wright and Randall. The region thus included extends from 74 cm^{-1} to 560 cm^{-1} and contains some 173 lines. Since the average spacing between the lines is only 2.7 cm^{-1}, it is evident that the success and completeness of an analysis depends upon experimental data of high accuracy and resolution such as are now for the first time available.

1. Calculation of the energy levels

The starting point of this work rests upon the investigation of the vibration rotation bands of water vapor made by Mecke[4] and his collaborators. They have determined 42 of the rotational energy levels of the nonvibrating molecule including the states from $J=0$ to $J=4$ together with a few of the higher levels. A preliminary study showed that the rotation lines predicted from their levels were in most cases in good agreement with the positions of certain of the lines observed in the far infrared spectrum. It was therefore concluded that the moments of inertia deduced by them might be taken as substantially correct. This is the essential key without which the analysis would be impossible, for, through the moments of inertia the energy levels of the asymmetrical rotator may be calculated. The calculated levels then form the guides in determining the actual energy levels whose differences will give the rotation lines.

It was found convenient to employ the equations obtained by Nielsen[5] from the Wang secular determinant. In the course of the work a number of errors in Nielsen's equations were located. Professor Nielsen has subsequently informed us that these errors were typographical in nature. The list of corrections which he kindly sent us agrees with ours and is as follows.

$J=6$

2nd equation

$+4725b$ in the constant coefficient should be $-4725b$.

4th equation

$-636b^2$ in the coefficient of W^2 should be $-1176b^2$

$-34144b^2$ in the coefficient of W should be $-53664b^2$.

$J=9$

1st equation

-147456 in the constant coefficient should be $+147456$.

2nd equation

$+7056b^2$ in the coefficient of W^3 should be $-7056b^2$.

3rd equation

$+822149b^4$ in the coefficient of W should be $+1822149b^4$

$-45052805b^4$ in the constant coefficient should be $-115052805b^4$.

4th equation

$+822149b^4$ in the coefficient of W should be $+1822149b^4$

$-189344780b^2$ in the constant coefficient should be $+189344790b^2$

$-45052805b^4$ in the constant coefficient should be $-115052805b^4$.

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[3] R. B. Barnes, W. S. Benedict, and C. M. Lewis, Phys. Rev. **47**, 918 (1935).

[4] R. Mecke, W. Baumann, and K. Freudenberg, Zeits. f. Physik **81**, 313, 445, 465 (1933).

[5] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

$J=10$

1st equation

$+23531860b^3$ in the coefficient of W should be $+23457060b^3$.

2nd equation

$-23531860b^3$ in the coefficient of W should be $-23457060b^3$

-8903025 in the constant coefficient should be -893025.

4th equation

$+3177400320b^2$ in the coefficient of W should be $-3177400320b^2$

$-2697416640b^4$ in the coefficient of W should be $+2697416640b^4$.

We have also computed the equations which determine the levels of $J=11$. They are:

$$\begin{aligned}&W^5-220W^4+W^3(16368-8976b^2)\\&\quad-W^2(489280-1476288b^2)\\&\quad+W(5395456-70684416b^2+10644480b^4)\\&\quad-14745600+956421120b^2-739307520b^4=0.\end{aligned}$$

$$\begin{aligned}&W^6-220W^5+W^4(16368-17556b^2)\\&\quad-W^3(489280-3329568b^2)\\&\quad+W^2(5395456-203708736b^2+55226160b^4)\\&\quad-W(14745600-4622346240b^2+6741051840b^4)\\&\quad-3162931200b^2+183417062400b^4-15437822400b^6=0.\end{aligned}$$

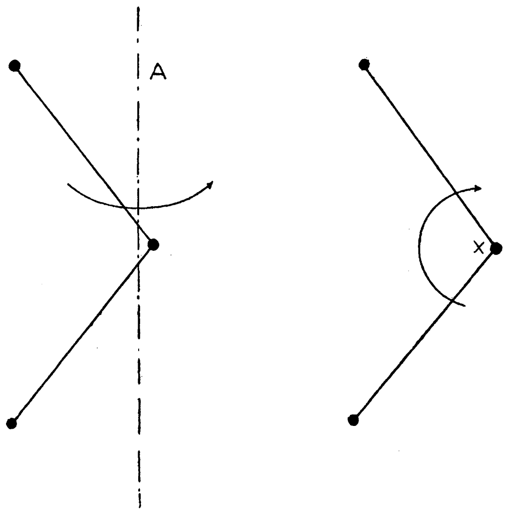
$$\begin{aligned}&W^6-W^5(286\mp 66b)+W^4(28743\mp 18810b-11121b^2)\\&\quad-W^3(1234948\mp 1878228b-2660724b^2\pm 463716b^3)\\&\quad+W^2(21967231\mp 79628340b-206124534b^2\\&\quad\pm 100549548b^3+20148975b^4)-W(128816766\\&\quad\mp 1370208906b-5931201876b^2\pm 648367671 6b^3\\&\quad+3161391030b^4\mp 339022530b^5)+108056025\\&\quad\mp 7131697650b-5101515094 5b^2\pm 122077531620b^3\\&\quad+107896714695b^4\mp 33414581970b^5-2170943775b^6=0.\end{aligned}$$

The numerical values which were chosen for the moments of inertia are $h/8\pi^2cA=27.8055$, $h/8\pi^2cB=14.499724$, $h/8\pi^2cC=9.279276$. These figures were made to differ slightly from those given by Mecke since by so doing the parameter of asymmetry b which enters the algebraic equations becomes the simple number -0.164, thus facilitating the numerical work. It must be emphasized that the moments of inertia just given are not in any way more accurate than those found by Mecke. They simply represent a definite zeroth order approximation and will form a starting point for further calculations.

Our results appear in Table I in the following form. The fourth column gives the actual values for the energy levels as obtained from the observed lines while the first column gives the amount by which the observed level is lower than the computed level. Thus the energy levels as determined from the asymmetrical rotator formulae using the above moments of inertia are given by the sum of the numbers appearing in columns one and four of Table I.

An inspection of this table reveals that the differences recorded in column one are often large, ranging as high as 279.19 cm^{-1} for the level 11_{11} although they are much smaller for the lower levels of each J group. While these differences are in part due to the fact that the moments of inertia chosen are not the true moments, they represent principally the change in energy caused by the centrifugal forces of the rotation. That is, the water molecule is not completely rigid but is slightly distorted by its rotation. We intend to consider this point more exactly in a future paper but for the present we would like to calculate the order of magnitude of the stretching and its effect upon the levels.

The water molecule is, of course, an asymmetrical rotator and any exact theory of the centrifugal distortion must start from this point. However, the highest τ states of any J group correspond in fairly good approximation to a simple spinning of the molecule about the axis of least moment of inertia A as indicated in Fig. 2a. The rotational energy in this approximation is $h^2J^2/8\pi^2A$ according to which the energy of the level 10_{10} for example would be 2781 cm^{-1} whereas the exact formula gives the value 2902 cm^{-1}; an error of 4 percent. It is most convenient to specify the positions of the nuclei in the rotating molecule by means of the displacement coordinates q, x and y where q is the change in distance between the two hydrogen



(a) (b)

FIG. 2. The water molecule.

TABLE I. *The rotational energy levels of the water molecule.*

δW		J_τ	W	δW		J_τ	W	δW		J_τ	W	δW		J_τ	W
0	+ +	0_0	0	28.46	− +	6_5	1045.34	3.00	− −	8_{-6}	883.12	3.00	+ −	10_{-9}	1114.91
				12.83	− −	6_4	888.89	1.32	+ −	8_{-7}	744.31	3.00	+ +	10_{-10}	1114.91
0.01	+ −	1_1	42.30_c	12.83	+ −	6_3	888.85	1.32	+ +	8_{-8}	744.24				
.02	− −	1_0	37.06_c	5.05	+ +	6_2	757.84					279.19	+ −	11_{11}	3218.55
.00	− +	1_{-1}	23.78_c	4.92	− +	6_1	756.90	134.90	+ −	9_9	2226.41	279.19	− −	11_{10}	3218.55
				2.29	− −	6_0	661.63	134.90	− −	9_8	2226.41	193.68	− +	11_9	2974.88
.16	+ +	2_2	136.10	1.80	+ −	6_{-1}	649.11	84.29	− +	9_7	2010.67	193.68	+ +	11_8	2974.88
.19	− +	2_1	134.81	2.08	+ +	6_{-2}	602.78	84.29	+ +	9_6	2010.67	130.06	+ −	11_7	2741.42
.04	− −	2_0	95.04_c	1.30	− +	6_{-3}	553.00	49.64	+ −	9_5	1811.18	130.06	− −	11_6	2741.42
.04	+ −	2_{-1}	79.38_c	1.50	− −	6_{-4}	542.80	49.64	− −	9_4	1811.18	83.77	− +	11_5	2523.08
.05	+ +	2_{-2}	70.03_c	.51	+ −	6_{-5}	447.20	27.57	− +	9_3	1631.95	83.77	+ +	11_4	2523.08
				.54	+ +	6_{-6}	446.69	27.57	+ +	9_2	1631.81	52.51	+ −	11_3	2322.82
1.38	+ −	3_3	285.45					15.66	+ −	9_1	1477.78	52.47	− −	11_2	2322.77
1.37	− −	3_2	285.26	52.05	+ −	7_7	1395.26	15.47	− −	9_0	1475.46	33.80	− +	11_1	2145.17
.15	− +	3_1	212.07	52.05	− −	7_6	1395.26	11.65	− +	9_{-1}	1360.85	33.26	+ +	11_0	2144.06
.09	+ +	3_0	206.25	27.20	− +	7_5	1216.63	10.21	+ +	9_{-2}	1340.98	25.74	+ −	11_{-1}	2000.71_c
.01	+ −	3_{-1}	173.33	27.20	+ +	7_4	1216.63	11.40	+ −	9_{-3}	1283.29	26.65	− −	11_{-2}	1984.20
.05	− −	3_{-2}	142.17	12.80	+ −	7_3	1060.07	6.79	− −	9_{-4}	1216.62	27.39	− +	11_{-3}	1898.56
.06	− +	3_{-3}	136.74	12.80	− −	7_2	1059.88	8.48	− +	9_{-5}	1202.28	22.39	+ +	11_{-4}	1840.14
				5.75	− +	7_1	931.50	3.89	+ +	9_{-6}	1080.72	25.36	+ −	11_{-5}	1811.21
5.21	+ +	4_4	488.24	5.68	+ +	7_0	927.92	4.20	+ −	9_{-7}	1079.41	14.26	− −	11_{-6}	1694.71
5.21	− +	4_3	488.24	4.00	+ −	7_{-1}	842.65	2.06	− −	9_{-8}	920.41	14.64	− +	11_{-7}	1691.13_c
1.21	− −	4_2	383.90	3.06	− −	7_{-2}	816.78	2.06	− +	9_{-9}	920.41	7.68	+ +	11_{-8}	1525.65
1.29	+ −	4_1	382.49	3.76	− +	7_{-3}	782.54					7.80	+ −	11_{-9}	1525.36
.38	+ +	4_0	315.66	1.76	+ +	7_{-4}	709.54	198.44	+ +	10_{10}	2703.28	4.33	− −	11_{-10}	1327.58
.13	− +	4_{-1}	300.33	2.03	+ −	7_{-5}	704.40	198.44	− +	10_9	2703.28	4.33	− +	11_{-11}	1327.58
.52	− −	4_{-2}	275.21	.82	− −	7_{-6}	586.53	131.51	− −	10_8	2472.44				
.12	+ −	4_{-3}	224.74	.84	− +	7_{-7}	586.32	131.51	+ −	10_7	2472.44		− −	12_6	3033.78
.28	+ +	4_{-4}	221.90					83.25	+ +	10_6	2255.08		+ −	12_5	3033.78
				86.75	+ +	8_8	1789.77	83.25	− +	10_5	2255.08		− +	12_{-9}	1775.26_c
13.50	+ −	5_5	742.30	86.75	− +	8_7	1789.77	50.25	− −	10_4	2055.04		− −	12_{-10}	1775.26_c
13.50	− −	5_4	742.30	50.12	− −	8_6	1591.47	50.25	+ −	10_3	2055.04		+ −	12_{-11}	1558.42
4.92	− +	5_3	610.42	50.12	+ −	8_5	1591.47	29.79	+ +	10_2	1876.16		+ +	12_{-12}	1558.42
4.89	+ +	5_2	610.21	27.07	+ +	8_4	1411.89	29.75	− +	10_1	1875.68				
1.45	+ −	5_1	508.86	27.07	− +	8_3	1411.89	18.87	− −	10_0	1726.23		+ +	13_{-10}	2042.99
1.45	− −	5_0	503.94	13.57	− −	8_2	1256.24	18.56	+ −	10_{-1}	1719.75		+ −	13_{-11}	2042.99
.88	− +	5_{-1}	446.52	13.59	+ −	8_1	1255.45	20.53	+ +	10_{-2}	1614.43		− −	13_{-12}	1807.36_c
.55	+ +	5_{-2}	416.02	7.89	+ +	8_0	1132.10	13.75	− +	10_{-3}	1581.88		− +	13_{-13}	1807.36_c
.73	+ −	5_{-3}	399.45	7.13	− +	8_{-1}	1123.11	16.70	− −	10_{-4}	1538.65				
.32	− −	5_{-4}	326.49	4.65	− −	8_{-2}	1052.92	9.67	+ −	10_{-5}	1446.68		+ −	14_{-13}	2074.30
.40	− +	5_{-5}	325.23	4.52	+ −	8_{-3}	1006.38	11.22	+ +	10_{-6}	1438.50		+ +	14_{-14}	2074.30
				5.89	+ +	8_{-4}	983.22	5.57	− +	10_{-7}	1294.07				
28.46	+ +	6_6	1045.34	2.56	− +	8_{-5}	885.84	5.73	− −	10_{-8}	1293.49				

atoms. x and y are the displacements of the oxygen atom relative to the center of gravity of the hydrogens $\|$ and $\perp$ to the A axis, respectively. Since the centrifugal forces for this simple spinning motion are always perpendicular to the A axis, it is clear that x will be uninfluenced by them. We may accordingly omit it from the calculations. The total energy, rotational plus potential, has the form,

$$W/hc = hJ^2/8\pi^2cA + \tfrac{1}{2}(ay^2 + bq^2 + 2dqy),$$

where a, b and d are potential constants whose values will be considered later. A is the moment of inertia of the rotating molecule and is equal to $2mM(y_0+y)^2/(2m+M)$, where y_0 is the distance between the oxygen and the line joining the hydrogens in the nonrotating molecule. The nature of the motion is evidently such that the coordinates q and y will possess constant values which may be found by setting the derivatives of W to zero.

Thus $\quad (1/hc)(\partial W/\partial q) = bq + dy = 0.$

Let this relation be used to eliminate q from the energy W and introduce the notation,

$$\alpha = h/8\pi^2\mu y_0^2 c,\quad \beta = (ab - d^2)y_0^2/2b \quad\text{and}\quad \eta = y/y_0,$$

then $\quad W/hc = \alpha J^2/(1+\eta)^2 + \beta\eta^2.$

The value of η is now obtained by differentiation and is a root of the equation,

$$\eta(1+\eta)^3 = \alpha J^2/\beta.$$

The change in energy due to the rotational stretching is the difference between W/hc and αJ^2 and is readily found to be

$$\delta W/hc = -\beta\eta^2(1+3\eta+\eta^2).$$

The change in energy just calculated is a rigorous consequence of the assumptions employed, namely simple spinning about the A axis and a potential energy expression involving only quadratic terms. If $\delta W \ll W$, the formula may be developed and only first-order terms retained, in which case

$$(\delta W)_0/hc = -\beta\eta^2 = -\alpha^2 J^4/\beta.$$

The numerical value of α is of course 27.8055 cm^{-1} and the distance y_0 is known from Mecke's work to be 0.5845×10^{-8} cm. The potential energy constants a, b, d may be found from Bonner's[6] analysis of the vibrational bands of water. The coordinates used by Bonner are the valence coordinates but a transformation from his constants to ours may easily be effected, for example, through the formulae given by Sutherland and Dennison.[7] Combining these quantities we find $\beta = 37{,}635$ cm^{-1}. The numerical values of $(\delta W)_0$ and of δW may now easily be computed and are listed in the second and third columns of Table II in the units of cm^{-1}. The fourth column represents the difference between the calculated energy levels of the asymmetrical rotator and the observed levels of the water molecule. It is thus apparent that the principal cause of the difference between the computed and observed levels is due to the centrifugal force stretching.

It is interesting to note that the first-order calculation $(\delta W)_0$ differs considerably from the exact calculation δW particularly for the larger J values. This is important since it shows that no first-order computation of the stretching effect, as for example that proposed by Wilson,[8] can possibly be adequate for values of δW much above 5 cm^{-1}. A second way of showing this is to point out that for the higher energies of rotation the centrifugal forces are so great that the distortion of the molecule is no longer small. Thus for $J=11$, the bond angle changes from its equilibrium value of 104° 36′ to 98° 52′ while the O–H distance changes from 0.9558A to 0.9640A.

The differences between δW and δW_{obs} arise from two causes, the principal one of which is that δW has been calculated from much too simple a model. The system must eventually be treated wave mechanically and also the influence of anharmonic terms in the potential must be considered. The second cause of the difference is that the asymmetric rotator energy levels have been calculated using what might be called trial moments of inertia. If δW were known exactly, then $\delta W - \delta W_{\text{obs}}$ would immediately furnish the appropriate corrections to the trial moments. No significance is to be attributed to the fact that $(\delta W)_0$ appears to agree with the observed differences better than δW.

The values which have just been considered apply to the highest levels of each J group. Similar calculations may be made on the lowest levels of each group where the motion approximates to a simple spinning about the greatest moment of inertia axis as shown in Fig. 2b. Since this moment is larger, the angular velocity is lower and the corrections turn out to be sufficiently small so that only the first order term $(\delta W)_0$ need be considered. This together with δW_{obs} is shown in the fifth and sixth columns of Table II. The agreement seems to be rather less good than that for the high levels, possibly due to the fact that the moments of inertia of the molecule are such that the low levels correspond to simple spinning about a principal axis less well than the higher levels.

TABLE II. *Numerical values of $(\delta W)_0$ and of δW.*

J	$(\delta W)_0$	δW	δW_{obs}	$(\delta W)_0$	δW_{obs}
0	0	0	0	0	0
1	0.02	0.02	0.02	0.00	0.00
2	0.33	0.33	0.18	0.00	0.04
3	1.66	1.63	1.38	0.02	0.05
4	5.26	5.08	5.21	0.06	0.20
5	12.84	12.18	13.50	0.14	0.36
6	26.62	24.72	28.46	0.30	0.52
7	49.33	44.67	52.05	0.55	0.83
8	84.15	74.18	86.75	0.95	1.32
9	134.79	115.40	134.90	1.52	2.06
10	205.44	170.52	198.44	2.31	3.00
11	300.78	241.68	279.19	3.38	4.33

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[6] L. G. Bonner, Phys. Rev. **46**, 458 (1934).

[7] G. B. B. M. Sutherland and D. M. Dennison, Proc. Roy. Soc. **148**, 250 (1935), see page 258.

[8] E. B. Wilson, Jr., J. Chem. Phys. **4**, 526 (1936).

TABLE III. *The rotation lines of water vapor.*

ν_{obs}	ν_{calc}	I	TRANSITION
554.97	555.00	(0.24)?	$7_4 - 6_0$
550.33			
548.04			
546.65	546.65	0.12	$11_{-4} - 10_{-8}$
545.70	545.70	(0.06)	$11_{-2} - 10_{-6}$
536.48	536.48	(0.26)?	$6_5 - 5_1$
526.23	526.27	0.79	$10_{-5} - 9_{-9}$
519.81			
518.09	518.09	0.26	$10_{-6} - 9_{-8}$
	517.47	(0.1)?	$10_{-1} - 9_{-5}$
517.14	517.14	0.34	$11_{-5} - 10_{-7}$
515.27	515.27	0.04	$11_{11} - 10_9$
			$11_{10} - 10_{10}$
510.70	510.70	0.07	$12_5 - 11_5$
			$12_6 - 11_4$
507.10	507.07	?	$7_3 - 6_{-3}$
502.45	502.47	(0.7)?	$10_{-3} - 9_{-7}$
	502.44	0.10	$11_9 - 10_7$
			$11_8 - 10_8$
492.22	492.24	(0.4)	$9_0 - 8_{-4}$
486.34	486.34	0.24	$11_7 - 10_5$
			$11_6 - 10_6$
484.18			
481.28			
478.05			
476.87	476.87	0.30	$10_{10} - 9_8$
			$10_9 - 9_9$
472.68	472.38	0.62	$9_{-4} - 8_{-8}$
468.88			
468.04	468.04	0.56	$11_5 - 10_3$
			$11_4 - 10_4$
461.77	461.77	0.75	$10_8 - 9_6$
			$10_7 - 9_7$
458.05	457.97	1.78	$9_{-5} - 8_{-7}$
	457.93	(1.0)?	$10_{-4} - 9_{-6}$
	457.86	(0.45)	$9_{-2} - 8_{-6}$
	457.10	(0.1)?	$7_2 - 6_{-2}$
453.96			
451.88	451.88	0.30	$11_{-3} - 10_{-5}$
447.14	447.14	0.84	$11_3 - 10_1$
446.61	446.61	0.28	$11_2 - 10_2$
443.90	443.90	1.8	$10_6 - 9_4$
			$10_5 - 9_5$
442.24	442.33	(4.0)?	$6_3 - 5_{-1}$
436.64	436.64	2.0	$9_9 - 8_7$
			$9_8 - 8_8$
434.98			
431.35	431.35	?	$6_2 - 5_{-4}$
429.09	429.00	?	$10_1 - 10_{-5}$
426.42	426.64	(0.1)?	$5_4 - 4_0$
425.42	425.42	1.5	$11_1 - 10_{-1}$
423.14	423.14	3.4	$10_4 - 9_2$
			$10_3 - 9_3$
420.10	420.06	3.9	$8_{-3} - 7_{-7}$
419.20	419.20	4.6	$9_7 - 8_5$
			$9_6 - 8_6$
418.68	418.71	(2.2)	$8_{-1} - 7_{-5}$
417.88	417.83	0.5	$11_0 - 10_0$
400.70	400.70	1.5	$10_2 - 9_0$
399.29	399.29	9.1	$9_5 - 8_3$
			$9_4 - 8_4$
397.81	397.90	4.4	$10_1 - 9_1$
	397.81	(2.2)	$10_{-2} - 9_{-4}$
	397.45	(2.5)?	$9_{-3} - 8_{-5}$
396.79	396.69	1.2	$8_{-4} - 7_{-6}$
394.51	394.51	11	$8_8 - 7_6$
			$8_7 - 7_7$
385.58	385.68	?	$5_3 - 4_{-3}$
385.17	385.25	(1.6)	$10_0 - 9_{-2}$
	385.12	(1.8)	$7_0 - 6_{-4}$
384.21			
380.45			
378.60	378.80	?	$8_{-1} - 8_{-7}$
376.57	376.50	12	$9_3 - 8_1$
375.54	375.57	3.9	$9_2 - 8_2$
374.80	374.84	22	$8_6 - 7_4$
			$8_5 - 7_5$
370.26	370.09	2.5	$7_{-2} - 6_{-6}$
	369.77	0.6	$11_{-2} - 10_{-2}$
358.90	358.90	(6.2)	$10_{-1} - 9_{-1}$
357.45	357.45	(10)	$6_1 - 5_{-3}$
354.67	354.67	18	$9_1 - 8_{-1}$
354.47	354.47	(15)	$9_{-1} - 8_{-3}$
351.88	352.01	9	$8_4 - 7_2$
	351.82	27	$8_3 - 7_3$
349.92	349.92	44	$7_7 - 6_5$
			$7_6 - 6_6$
346.06	346.07	?	$4_4 - 3_{-2}$
343.38	343.38	(16)	$8_{-2} - 7_{-4}$
	343.36	5.5	$9_0 - 8_0$
335.34	335.34	6.5	$7_{-3} - 6_{-5}$
	335.00	(0.4)?	$5_2 - 4_{-2}$
328.34	328.32	13	$8_2 - 7_0$
327.78	327.77	74	$7_5 - 6_3$
			$7_4 - 6_4$
323.90	323.95	39	$8_1 - 7_1$
	323.88	(6)	$6_{-1} - 5_{-5}$
315.32	315.32	19	$8_0 - 7_{-2}$
	314.91	(1.6)?	$4_3 - 3_{-1}$
305.00			
303.30	303.17	80	$7_3 - 6_1$
303.00	303.04	135	$6_6 - 5_4$
			$6_5 - 5_5$
302.04	302.04	27	$7_2 - 6_2$
	301.49	0.7	$11_{-4} - 10_{-4}$
298.61	298.59	(6)	$10_{-3} - 9_{-3}$
290.91			
289.65	289.65	140	$7_{-1} - 6_{-3}$
	288.06	(2)	$9_{-2} - 8_{-2}$
282.45	282.39	102	$7_1 - 6_{-1}$
	282.04	(3)	$5_0 - 4_{-4}$
280.46	280.46	42	$8_{-1} - 7_{-1}$
278.55	278.68	47	$6_4 - 5_2$
	278.43	142	$6_3 - 5_3$
276.29	276.29	(35)	$6_{-2} - 5_{-4}$
267.73	267.73	1.5	$13_{-11} - 12_{-9}$
			$13_{-10} - 12_{-10}$
266.94	266.94	1.5	$14_{-14} - 13_{-12}$
			$14_{-13} - 13_{-13}$
266.29	266.29	30	$7_0 - 6_0$
256.21	256.21	1.4	$11_{-6} - 10_{-6}$
254.06	254.06	300	$5_5 - 4_3$
			$5_4 - 4_4$
	253.90	57	$6_2 - 5_0$
	249.90	3.2	$12_{-9} - 11_{-9}$
	249.61	1.1	$12_{-10} - 11_{-8}$
	248.94	4.3	$13_{-13} - 12_{-11}$
			$13_{-12} - 12_{-12}$
248.01	248.04	160	$6_1 - 5_1$
245.65	245.75	(9)	$4_1 - 3_{-3}$
	245.61	(60)	$6_0 - 5_{-2}$
244.46	244.40	11	$10_{-5} - 9_{-5}$
233.40	233.40	(6.5)	$9_{-4} - 8_{-4}$
232.16	232.16	3	$11_{-8} - 10_{-8}$
231.29	231.29	8	$11_{-9} - 10_{-7}$
230.84	230.84	11	$12_{-12} - 11_{-10}$
			$12_{-11} - 11_{-11}$
	229.33	(0.8)	$11_{-5} - 10_{-3}$
227.93	227.93	250	$5_3 - 4_1$
226.38	226.31	83	$5_2 - 4_2$
223.82	223.84	(50)	$8_{-3} - 7_{-3}$
221.74	221.88	3	$10_{-6} - 9_{-4}$
	221.78	(110)	$5_{-1} - 4_{-3}$
	217.36	.02	$10_8 - 10_6$
			$10_7 - 10_5$
	215.74	.03	$9_9 - 9_7$
			$9_8 - 9_6$
215.31	215.23	(1.4)?	$3_2 - 2_{-2}$
214.70	214.66	18	$10_{-7} - 9_{-7}$
214.00	214.00	23	$7_{-2} - 6_{-2}$
212.68	212.77	6	$10_{-8} - 9_{-6}$
	212.67	25	$11_{-11} - 10_{-9}$
			$11_{-10} - 10_{-10}$
208.53	208.53	260	$5_1 - 4_{-1}$
203.12	202.98	110	$4_4 - 3_2$
202.79	202.79	330	$4_3 - 3_3$
202.55	202.59	(140)	$6_{-1} - 5_{-1}$
200.44	200.04	0.05	$10_6 - 10_4$
			$10_5 - 10_3$
199.31	199.49	0.1	$9_7 - 9_5$
			$9_6 - 9_4$
	198.30	0.2	$8_8 - 8_6$
			$8_7 - 8_5$
	198.07	0.3	$11_{-8} - 11_{-10}$
197.62	197.74	0.9	$11_{-9} - 11_{-11}$
	197.67	(0.8)	$10_{-4} - 9_{-2}$
	197.60	12	$9_{-6} - 8_{-6}$
195.88	195.90	(9)	$9_{-5} - 8_{-3}$
194.47	194.50	50	$10_{-9} - 9_{-9}$
			$10_{-10} - 9_{-8}$
193.57	193.57	35	$9_{-7} - 8_{-5}$
188.28	188.28	68	$5_0 - 4_0$
183.58	183.63	?	$5_1 - 5_{-5}$
181.46	181.44	67	$8_{-5} - 7_{-5}$
	179.58	0.7	$8_6 - 8_4$
			$8_5 - 8_3$
	179.37	0.1	$9_4 - 9_2$
	179.36	0.1	$10_3 - 10_1$
	179.23	0.3	$9_5 - 9_3$
179.12	179.16	1.3	$10_{-7} - 10_{-9}$
	178.88	0.03	$10_4 - 10_2$
178.62	178.63	1	$7_7 - 7_5$
			$7_6 - 7_4$
	178.58	0.4	$10_{-8} - 10_{-10}$
177.65	177.65	100	$4_2 - 3_0$
176.12	176.12	90	$9_{-8} - 8_{-8}$
			$9_{-9} - 8_{-7}$
173.50	173.58	20	$8_{-6} - 7_{-4}$
	173.49	(50)	$4_0 - 3_{-2}$
170.40	170.42	270	$4_1 - 3_1$
169.56	169.06	0.1	$11_{-6} - 11_{-8}$
166.78	166.74	35	$7_{-4} - 6_{-4}$
166.32	166.44	(7)	$8_{-4} - 7_{-2}$
161.90	162.00	?	$4_2 - 4_{-4}$
160.21	160.31	0.9	$9_{-6} - 9_{-8}$
	160.18	(3)	$9_{-3} - 8_{-1}$
158.96	159.00	2.7	$9_{-7} - 9_{-9}$
158.00	157.99	107	$8_{-7} - 7_{-7}$
157.70	157.71	36	$8_{-8} - 7_{-6}$
	156.75	0.8	$7_4 - 7_2$
	156.56	2.4	$7_5 - 7_3$
156.49	156.47	4	$6_6 - 6_4$
			$6_5 - 6_3$
	156.44	1.3	$8_3 - 8_1$
	156.35	0.2	$9_2 - 9_0$
155.62	155.93	0.2	$10_1 - 10_{-1}$
	155.65	0.4	$8_4 - 8_2$
	154.17	0.5	$9_3 - 9_1$
153.55	153.55	(130)	$6_{-3} - 5_{-3}$
152.55	152.61	0.8	$10_{-5} - 10_{-7}$

TABLE III.—*Continued.*

ν_{obs}	ν_{calc}	I	TRANSITION	ν_{obs}	ν_{calc}	I	TRANSITION	ν_{obs}	ν_{calc}	I	TRANSITION
151.37	151.40	88	$7_{-5}-6_{-3}$		124.36	0.4	$9_{-2}-9_{-4}$		99.04	40	2_2-1_0
150.62	150.64	290	3_3-2_1		124.12	0.7	8_2-8_0		98.84	(6)	$6_{-2}-5_0$
	149.93	0.1	10_2-10_0	122.95	123.01	3	$7_{-4}-7_{-6}$		96.21	3	6_2-6_0
149.15	149.16	95	3_2-2_2		122.87	1.5	$9_{-5}-9_{-7}$	96.12	96.11	(17)	$6_{-1}-6_{-3}$
144.81	145.01	0.3	$10_{-6}-10_{-8}$	121.97	121.97	180	$6_{-5}-5_{-5}$		96.11	4	$6_{-4}-6_{-6}$
141.50	141.53	5.4	$8_{-5}-8_{-7}$		120.54	3.7	$8_{-3}-8_{-5}$		94.42	(0.03)	10_0-9_2
140.81	140.81	65	$5_{-2}-4_{-2}$	120.20	120.20	60	$6_{-6}-5_{-4}$	92.51	92.51	124	2_1-1_1
139.84	139.84	50	$7_{-6}-6_{-6}$	118.08	118.08	8	$7_{-5}-7_{-7}$	89.53	89.53	6	$5_{-2}-5_{-4}$
139.09	139.12	150	$7_{-7}-6_{-5}$		116.93	0.7	9_1-9_{-1}	88.42	88.85	5	7_1-7_{-1}
	138.97	(0.1)	$10_{-2}-9_0$	116.74	116.73	4	$8_{-1}-8_{-3}$	88.00	88.00	165	$4_{-3}-3_{-3}$
	138.88	1.7	$8_{-6}-8_{-8}$		111.80	0.3	10_0-10_{-2}		87.92	9	5_0-5_{-2}
138.09	137.87	0.4	$10_{-1}-10_{-3}$	111.21	111.21	51	3_0-2_0		85.83	(0.04)	$10_{-5}-9_{-1}$
	135.90	0.6	$9_{-4}-9_{-6}$		111.18	2	7_0-7_{-2}	85.62	85.75	(3)	$7_{-1}-6_1$
	135.20	0.4	$10_{-3}-10_{-5}$	107.92	107.79	13	6_1-6_{-1}		84.75	0.02	$9_{-2}-8_2$
	134.48	0.3	9_0-9_{-2}	107.30	107.24	2.4	$7_{-2}-7_{-4}$		84.51	(0.04)	$9_{-4}-8_0$
133.45	133.43	(20)	$7_{-3}-6_{-1}$		106.27	6	5_2-5_0	82.16	82.16	30	4_1-4_{-1}
132.69	132.69	(150)	3_1-2_{-1}	105.78	105.80	13	$6_{-3}-6_{-5}$		81.01	0.6	$9_{-3}-9_{-5}$
	132.34	2.4	8_1-8_{-1}		105.75	17	4_3-4_1	79.59	79.73	45	$4_{-4}-3_{-2}$
	132.09	3.0	5_4-5_2		105.40	(0.5)	$9_{-1}-8_1$		79.18	0.5	8_0-8_{-2}
131.89	131.96	1.6	7_2-7_0	104.59	104.59	60	$5_{-4}-4_{-4}$	79.02	79.01	8	3_2-3_0
	131.95	7.9	6_3-6_1		104.34	5	4_4-4_2	78.26	78.14	4	$7_{-3}-7_{-5}$
	131.88	8.8	5_5-5_3		104.10	0.07	$10_{-3}-9_1$		77.56	0.5	$9_{-1}-9_{-3}$
130.90	131.05	2.6	6_4-6_2	101.46	101.56	16	5_3-5_1		75.78	0.04	$10_{-2}-10_{-4}$
128.64	128.57	4.6	7_3-7_1	100.59	100.49	180	$5_{-5}-4_{-3}$	75.59	75.59	20	$4_{-1}-4_{-3}$
126.96	127.00	(160)	$4_{-1}-3_{-1}$		100.15	0.1	$10_{-4}-10_{-6}$		74.88	0.7	$8_{-3}-7_1$
126.61	126.78	35	$6_{-4}-5_{-2}$		100.10	1	$8_{-4}-8_{-6}$	74.22	74.22	13	$5_{-3}-5_{-5}$
	125.00	(1)	$8_{-2}-7_0$	99.04	99.12	96	$5_{-3}-4_{-1}$				

2. The intensities of the rotation lines

The first step towards making an analysis is now complete. We are furnished with the energy levels of an asymmetrical molecule whose moments of inertia closely approximate those of water. The order of magnitude of the centrifugal stretching has been calculated for the highest and lowest levels and presumably will lie between these two limits for the intervening levels. The selection rules governing the allowed transitions of the asymmetric rotator are well known.[9] Each level is given a symbol, $(++)$, $(+-)$, $(-+)$ or $(--)$, which denotes the symmetry group to which the level belongs. If the electric moment lies along the middle axis of inertia, as it does in water vapor, the only radiative transitions are those connecting the levels $(++)\longleftrightarrow(--)$ or $(+-)\longleftrightarrow(-+)$. In addition to this $\Delta J=\pm 1$ or 0. The formula for the intensity of the line corresponding to the transition from the state $J_{\tau''}''$ to the state $J_{\tau'}'$ may be readily obtained.

$$I_{J'}{}^{J''}{}_{\tau'}{}^{\tau''}=(8\pi^3\nu N_{J''\tau''}/3hc)\times(1-e^{-h\nu/kT})(M_{J'}{}^{J''}{}_{\tau'}{}^{\tau''})^2.$$

In this expression ν is the frequency of the line and $N_{J''\tau''}$ is the number of molecules per cc in the initial state. It has the form

$$N_{J\tau}=(Ng_{J\tau}e^{-W_{J\tau}/kT})/\sum g_{J\tau}e^{-W_{J\tau}/kT},$$

where N is the total number of water molecules and $g_{J\tau}$, the weight of the state, is equal to $(2J+1)f$. The factor f is due to the existence of the hydrogen nuclear spin of $\frac{1}{2}(h/2\pi)$ and is equal to 3 for τ odd and 1 for τ even.

The quantity $M_{J'}{}^{J''}{}_{\tau'}{}^{\tau''}$ is the matrix element of the electric moment associated with the transition and may be calculated from the minors of the secular energy determinant of the asymmetric rotator. Such calculations were made earlier by one of us (D.M.D.) for the matrix elements connecting all the states up to and including $J=3$. The resulting expressions were algebraic functions of the asymmetry parameter b whose complexity increased so rapidly with J that it seemed inadvisable to attempt to extend them to higher J values. Moreover a study of those matrix elements which were determined revealed that they could usually be satisfactorily approximated in the following manner. The levels of an asymmetric rotator may be divided

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[9] See, for example, D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

roughly into two main classes and an intervening region. The first class in any J group are characterized by large τ values and the levels tend to associate themselves in pairs. The association becomes less marked as τ decreases. This class of levels corresponds to a rotation of the molecule about the axis of least moment of inertia together with the accompanying precession and nutation. The energies and wave functions are quite well approximated by symmetrical rotator energies and wave functions. Thus for water vapor the levels of $J=10$ from $\tau=10$ to $\tau=-1$ belong to the first class. The second class of levels extends upwards from the lowest τ values and corresponds to rotations about the greatest moment of inertia axis. In the present example they would include the levels from $\tau=-10$ to $\tau=-5$. The region between these classes corresponds roughly to rotations about the middle axis and is not well approximated by symmetrical rotator wave functions. The point of this discussion is that a matrix element connecting two levels belonging to the same class was found to differ very little from the corresponding matrix element of a symmetrical rotator. The numbering of the asymmetrical and symmetrical rotator levels is of course quite different and care must be used in selecting the proper indices. Thus in the first class of levels the indices $\tau=J$ and $J-1$ are to be identified with $K=J$ of the symmetric rotator and $\tau=J-2$ and $J-3$ with $K=J-1$ etc. In the second class $\tau=-J$ and $-J+1$ becomes $K=J$. When a transition occurs from a level of one class to that of another or to the intervening region, we have calculated the intensity as from each class separately and taken an average value. The approximation appears to be somewhat rough but it has proved a guide in identifying many lines and it will be seen later that our calculated intensities are usually in good agreement with those observed.

The formulae governing the intensities may now be given in explicit form providing we adopt the approximation of using the matrix elements derived from symmetric rotator wave functions.[9] It is convenient to divide them into three classes.

$$I_J{}^{J-1}{}_K{}^{K-1}=(CF\nu/c)e^{-W_{J-1,\ K-1}/kT}(1-e^{-h\nu/kT})\times(J+K)(J+K-1)/J, \quad \text{(a)}$$

$$I_J{}^{J-1}{}_K{}^{K+1}=(CF\nu/c)e^{-W_{J-1,\ K+1}/kT}(1-e^{-h\nu/kT})\times(J-K)(J-K-1)/J, \quad \text{(b)}$$

$$I_J{}^{J}{}_K{}^{K-1}=(CF\nu/c)e^{-W_{J,\ K-1}/kT}(1-e^{-h\nu/kT})\times(2J+1)(J+K)(J-K+1)/J(J+1). \quad \text{(c)}$$

The factor F is equal to $\frac{1}{4}$ or $\frac{3}{4}$ according as the subscripts τ are even or odd, respectively. The constant

$$C=4\pi^3NM_0{}^2/3h\sum g_{J\tau}e^{-W_{J\tau}/kT},$$

where M_0 is the permanent electric moment of the water molecule. In the present paper no attempt will be made to evaluate the absolute intensities of the lines although a preliminary calculation shows them to be of the right order of magnitude. The numbers appearing in Table III under the heading I are in reality the absolute intensities divided by the constant C. It may be of value to give one or two examples of these calculations in detail. Consider the line $5_3-5_1=101.46$. A study of the levels shows that both the initial and final states belong to one class of levels, namely, those corresponding to rotations about the least moment of inertia axis. Since $\Delta J=0$ the formula (c) must be used with $J=5$, $K=4$ and $F=\frac{3}{4}$. The resulting substitution yields $I=16.2C$.

The majority of the lines correspond to transitions from a level of one class to a level of the same class and for these our approximation should be well justified. These intensities are listed without braces. In the remaining cases, where the numbers are enclosed with braces, an interpolation of uncertain validity has been made. The line $6_{-2}-5_{-4}=276.29$ is such a one. If this is considered to be a transition between two levels belonging to rotations about the least moment of inertia axis then formula (a) should be employed with $J=6$, $K=2$ and $F=\frac{1}{4}$ giving $I=96.4C$. Such an interpretation would require the levels 6_{-2}, 6_{-3} and 5_{-3}, 5_{-4} to form close pairs. This is obviously false, particularly in the latter case. If we proceed under the assumption that the levels belong to the class of rotations about the greatest axis then formula (b) is applicable with $J=6$, $K=4$, $F=\frac{1}{4}$ and $I=3.4C$. This requires that 6_{-1}, 6_{-2} and 5_{-4}, 5_{-5} form pairs, a condition which is well met in the second case but badly fulfilled in the first. Thus neither calculation is satisfactory although the latter is apparently to be preferred. Accordingly this intensity is listed as $\frac{1}{3}[96.4+2(3.4)]C=(34)C$. It is clear that the intensities in braces are merely to be regarded as estimates which in extreme cases may be in error by factors as high as ten. In a few cases the symmetric rotator approximation is completely uncertain and these are denoted by placing a question mark behind the brace.

3. The rotational energy levels

It is now possible to construct the energy levels of the water molecule beginning with $J=0$ and working successively towards higher J values. The results are listed in Table I. The six levels, 1_1, 1_0, 1_{-1}, 2_0, 2_{-1} and 2_{-2}, are followed by the letter c which means that they have been calculated using the moments of inertia given by Mecke.[4] A correction for the centrifugal stretching has been applied which was based on Wilson's[8] equations. The necessity for calculating these levels lies in the fact that the lines which would fix their values fall in the far infrared outside the region experimentally measured. It seems impossible, however, that our estimates could be in error by more than a very few hundredths of waves per cm.

All the subsequent levels are derived from the observed lines by means of the following procedure. The position of an unknown level is approximately determined by subtracting a suitable correction from its computed value. The lines which connect this level with levels already known are then calculated and compared with the observed lines in the spectrum. For example, consider that point where the levels up through $J=5$ have been obtained. The two levels 6_6 and 6_5, as calculated from the asymmetric rotator formula, are practically coincident at 1073.76 cm^{-1}. The δW for $J=6$ was 24.72 and hence our first estimate for their position is 1049. There are only two transitions to $J=5$ levels, namely, a strong line $\left\{\begin{matrix}6_6-5_4\\6_5-5_5\end{matrix}\right\}$ and a weak line 6_5-5_1. Our initial estimates of these lines are accordingly 307 and 540 cm^{-1}. Turning to the spectrum we find a very strong line at 303.00 cm^{-1} and a weak line at 536.48, cm^{-1}. Identifying these with the transitions in question we obtain $\left\{\begin{matrix}6_6\\6_5\end{matrix}\right\}=1045.30$ and 1045.34, respectively. In this particular case it was felt that the weak line could be measured with slightly greater experimental accuracy and therefore the latter value was given preference. The next levels 6_4 and 6_3 are calculated to lie at 901.72 and 901.68. The δW is here estimated by observing that the δW of a next highest pair of one J group is about equal to the δW of the highest pair of the group $J-1$. This would put 6_4 and 6_3 at about 888 cm^{-1}. There are now three lines which correspond to the transitions, $\left\{\begin{matrix}6_6-6_4\\6_5-6_3\end{matrix}\right\}$, $\left\{\begin{matrix}6_4-5_2\\6_3-5_3\end{matrix}\right\}$ and 6_3-5_{-1}. These lines may easily be identified with those observed at, 156.49, 278.55 and 442.24 cm^{-1}.

In theory each level may be determined by means of two or three lines but in many cases (nearly $\frac{2}{3}$ of the levels) some of the lines are either too weak, are overlayed by much stronger lines, or fall outside the region investigated. This is particularly true for the high J groups and in fact none of the lines to the levels 11_{-1} and 11_{-7} were satisfactorily observable and consequently these values are estimated only. The fact that a level can be fixed by each of several lines is equivalent to the existence of combination relations. We might give, as examples, the following:

$$\begin{array}{rr} 8_{-7}-7_{-7}=158.00 & 7_{-5}-7_{-7}=118.08\\ 8_{-5}-8_{-7}=141.50 & 8_{-5}-7_{-5}=181.46\\ \hline 299.50 & 299.54\end{array}$$

$$\text{and}\quad\begin{array}{rr} 7_{-3}-6_{-5}=335.34 & 7_{-7}-6_{-5}=139.09\\ 8_{-3}-7_{-3}=223.82 & 8_{-3}-7_{-7}=420.10\\ \hline 559.16 & 559.19\end{array}$$

The errors of 0.04 and 0.03, respectively, are to be distributed among four lines. This order of magnitude for the error is in accordance with what is revealed by a study of the experimental curves themselves, namely, that a sharp single line may be located to within 0.05 cm^{-1}.

The methods which have been outlined proved very satisfactory for identifying the lines and determining the energy levels. However, an additional process for correlating the lines was found which served as an important check on the

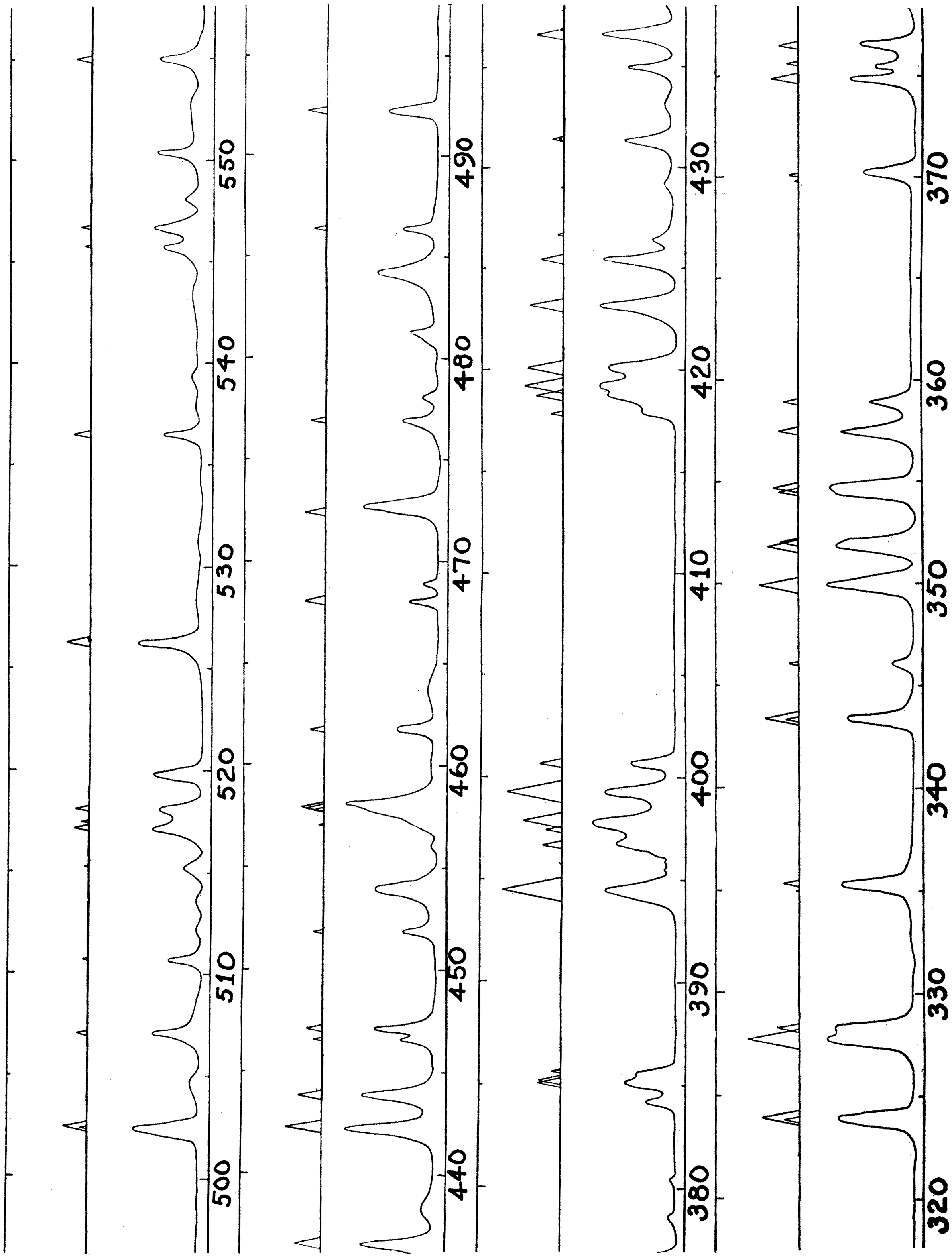

FIG. 3. Analysis of the rotational spectrum of water vapor.

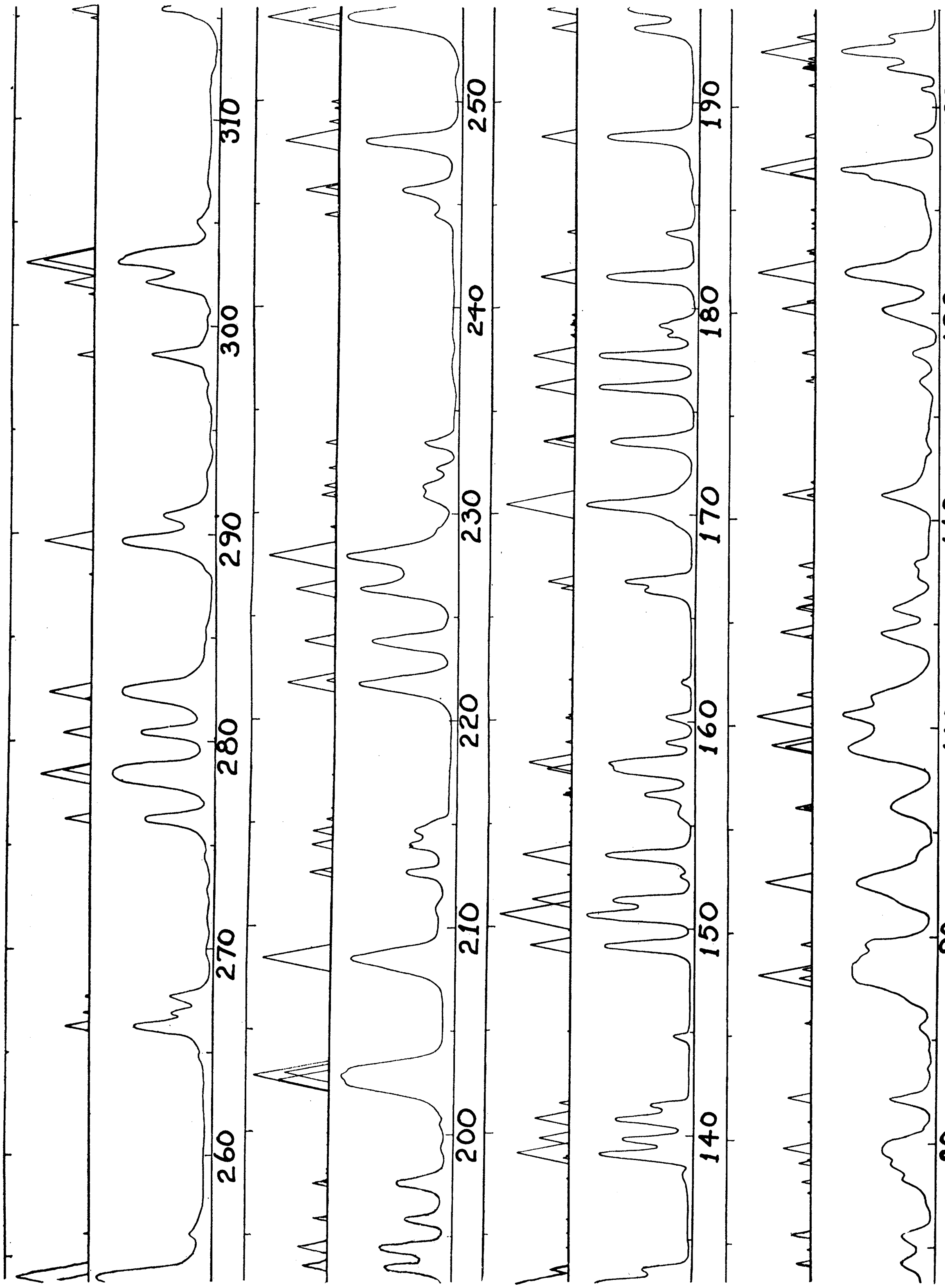

FIG. 4. Analysis of the rotational spectrum of water vapor.

identifications. This consisted in recognizing that many of the lines may be formed into series which are analytic in nature. As one example consider the transitions which connect the highest levels in one J group with the highest levels in the next lowest J group. The first observed members of this series are the two lines $2_1-1_1=92.51$ and $2_2-1_0=99.04$. An average value of these numbers, namely 95.78, is taken. There are ten members of the series of which the highest is $\left\{\begin{matrix}11_{11}-10_9\\11_{10}-10_{10}\end{matrix}\right\}=515.27$. The ten numbers are placed in a column and first and second differences are then taken. The second differences are found to have the values 1.03, 1.96, 2.17, 2.02, 2.33, 2.46, 1.90 and 1.83. The run of these numbers leaves no doubt but that the ten lines belong together and form a series. Second differences are of course very sensitive to changes in the frequencies of the original lines. For example the value 2.02 seems to be somewhat too low. It depends among others upon the line at 303.00 which is seen to be one component of a close doublet and hence rather inaccurately determined. If we should arbitrarily increase it to 303.08 then the third, fourth and fifth second differences would read 2.09, 2.18, 2.25; the others remaining unchanged. From the complete spectrum, in all six independent series were located, the longest containing ten numbers and the shortest, six. Other regularities exist between the energy levels which are revealed by a little inspection. The δW of one J group seems to be closely correlated with the δW of the next higher J group. Again from the highest level of a group to the lowest level δW decreases in a rather smooth manner except for a certain alternation. Thus starting from the bottom the δW of the 1st, 3rd etc. levels are high compared with the δW of the 2nd, 4th, etc., levels.

Through the use of the foregoing methods the rotational energy levels of water have been determined up through $J=11$. As a final test of our analysis we shall calculate the lines corresponding to every allowed transition together with the approximate expressions for the intensities. These are listed in Table III. A few of the lines connecting high energy states are not included in the table since their calculated intensities are so small as to show that they lie well below the limit of observation. There are certain transitions which are possible for the asymmetric rotator but which are forbidden in the corresponding symmetric rotator. The approximate intensity formulae are consequently not applicable to these lines and we have treated them as follows. In every case the frequency of the line was calculated and a search was made to see if it had been found experimentally. In the great majority of instances no line was observed showing that its intensity must be very small. Such transitions of which an example is $5_4-6_{-6}=295.61$ were omitted from the table. In a few cases, as $4_4-3_{-2}=346.07$, lines were observed and these are listed in the table with question marks for their intensities. These recorded lines are usually between levels of low J values where the asymmetric nature of the rotation is most pronounced and which are hence the most likely to appear.

The data contained in Table III are shown graphically in Figs. 3 and 4. The lower curve represents the observed spectrum of water vapor as obtained by averaging the points found from several independent runs over each line. Unfortunately the intensities of the lines are not determined with anything like the accuracy attained for their positions. The relative intensities of neighboring lines or groups of lines can usually be relied upon but the curve gives no measure of the strength of a line in one frequency range with that in another range. This is evident from the manner in which the data were obtained. For the region from 74 cm^{-1} to about 300 cm^{-1} the spectrometer case was kept as dry as possible with P_2O_5. From this point onward the dryer was gradually removed until for the highest frequencies open trays of water were placed in the spectrometer. Thus there can be no direct comparison between two lines at say 200 and 400 cm^{-1}.

Above the experimental curve we have plotted the calculated positions and intensities of the lines. These are drawn so that the area under each triangle is proportional to the intensities appearing in the table. Since the intensities in the experimental curve were being augmented in going toward shorter wave-lengths by admitting more water into the path, it was necessary to increase the theoretical intensities. This was done somewhat arbitrarily by letting the proportionality factor be 1 from 74 cm^{-1} to 295 cm^{-1}, 2 from 295 to 380, 20 from 380 to 465 and 80 from 465 to 560 cm^{-1}.

4. Discussion

The figures which we have obtained for the rotational energy, in general, agree well with the values published by Mecke,[4] particularly for the lower levels of each J group. In the case of the higher levels there exist differences occasionally as large as 1 or 2 cm^{-1}. It appears to us that the present measurements of the far infrared spectrum allow a very much more precise determination of the levels than is attainable from any study of the existing data on the near infrared bands.

A comparison of our results with those found by Barnes, Benedict and Lewis[3] is less satisfactory since it shows a lack of agreement of from 1 to 9 cm^{-1}. A second and a principal difference between the present investigation and those which have gone before it, is the completeness with which the energy levels have been obtained. Thus it will be possible now to determine such quantities as for example the Zustandsumme at room temperature with an accuracy of 0.1 percent or better.

Let us now consider the degree of completeness with which the rotational spectrum of water vapor has been analyzed and the accuracy with which the levels have been determined. Two points of view must be presented. The first of these might be termed, the verification of the level scheme through combination relations. Of the total of 173 lines, 160 are satisfactorily accounted for. From these 160 lines, 115 distinct levels have been calculated thus implying the existence of 45 combination relations. Thus in principle there should be 45 predicted lines which may be compared with measured lines. Actually these lines are not isolated since each level was found by averaging the values as determined from all the lines ending upon the level in question. Nevertheless the exactness with which the combination relations are fulfilled is evinced by the good agreement between the observed and calculated frequencies in Table III. The smallness of the differences is an index of the uncertainty to be ascribed to the energy levels. For the levels up through $J=7$ or 8, where most of the combination relations occur, the order of magnitude of the error almost certainly is less than 0.1 cm^{-1} while for no level will it be more than 0.4 cm^{-1}.

The second method of testing our results is based on the fact that the energy levels are not independent numbers to be chosen at random but that they form a closely related group. Their positions are fixed by the three moments of inertia together with a limited number of parameters which determine the centrifugal stretching correction. The circumstance that the levels of Table I obey these conditions, is shown by the regular behavior of the quantity δW. In most cases, the displacement of a level by as much as 1 or 2 cm^{-1} would introduce pronounced discontinuities in the series which may be formed from successive values of δW.

The essential consistency of the analysis is indicated by the excellent correlation between the observed and predicted spectrum as shown in Figs. 3 and 4. Every strong observed line has an accompanying strong predicted line. There is no single instance of a calculated line of measurable intensity which fails to appear in the experimental curve.[10] This, we regard as highly important. There are, on the other hand, six lines of medium intensity and seven weak lines which are not represented in the predicted spectrum. For the most part these lie towards the higher frequencies and undoubtedly are lines corresponding to transitions to the levels of $J=12$ or even 13. There would be no difficulty about postulating levels by means of which these 13 lines would be accounted for. This we have refrained from doing since from a few scattered levels of $J=12$ we could not observe those regularities in δW which have everywhere been considered essential to the analysis.[11]

The analysis of the rotational spectrum of

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[10] The one possible exception lies at 249 cm^{-1} where two weak lines are predicted which should presumably have been observed. The reason that they were not, appears evident from a study of the original curves which show that great care was taken in drying the spectrometer as well as possible in order to measure accurately the two strong lines at 248.04 and 254.05 while less attention was paid to the intervening region.

[11] Certain levels of $J=12$ and higher are indeed listed in Table I but these were determined from lines which are members of a series and about which there can be little doubt.

water vapor appears to be complete in the sense that the lines have been identified and the energy levels determined. The next step is, of course, to obtain with great precision the effective moments of inertia of the molecule. This will demand an adequate calculation of the rotational stretching effect, a problem which we now plan to attack. On the experimental side we are endeavoring to map the rotational spectrum of D_2O. An accurate knowledge of the effective moments of inertia of both H_2O and D_2O would do much towards making possible a precise determination of the true moments and hence of the dimensions of the molecule.

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Secondary Processes of Ionization in Mercury Vapor

BENJAMIN L. SNAVELY
*Princeton University, Princeton, New Jersey**

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The ionization occurring in mercury vapor as the result of the impact of electrons of energy less than 10.4 volts was studied by use of a tube containing a small filament, the emission of which was limited by space-charge. The ionization produced has been studied as a function of electron velocity, bombarding current and pressure of the mercury vapor. For electron velocities above 7 volts the data are in agreement with the assumption that the larger part of the ionization is the result of ionization of metastable atoms by electron impact. Critical potentials at 8.4 and 8.6 volts are identified with the configurations $5d^96s^26p\ {}^3P_1{}^0$ and $5d^{10}6s7p\ {}^3P_1{}^0$, respectively. Another critical potential at 6.9 volts is tentatively identified as the difference between the lower metastable level, $6s6p\ {}^3P_0{}^0$, and a negative energy level, $6p^2\ {}^3P_1$. Large numbers of negative ions were found in the neighborhood of 4.9 volts. It is suggested that ionization observed in this region is due to the simultaneous formation of a positive ion and a negative ion upon the collision of a 2^3P_0 atom with a 2^3P_1 atom.

INTRODUCTION

A QUANTITATIVELY plausible explanation of the origin of the ionization which must occur in a low voltage arc was first given by K. T. Compton[1] in terms of an initial excitation of the vapor by electron impact and subsequent ionization of the excited atoms by the impact of other electrons. Various experiments in which the ionization is produced under more exactly controlled conditions than exist within an arc have since been explained on the basis outlined by Compton. Thus Franck and Einsporn[2] found critical potentials in mercury vapor corresponding to the potentials necessary to ionize the metastable levels and Smyth and Compton[3] observed a decrease in the ionization potential of iodine when it was excited by radiation from a mercury arc. Kannenstine[4] and Marshall[5] attempted to observe a lowering of the ionization potentials in He and in Hg due to the presence of metastable atoms but it was shown by Pool[6] that their results were inconclusive.

Experiments on the photoionization of mercury vapor by λ2537, discovered by Steubing[7] and later studied by Rouse and Giddings,[8] Foote,[9] and Houtermans,[10] indicate that there is probably some other secondary process in addition to that outlined by Compton which may be of major importance at least at higher pressures. It has been definitely shown that ions are produced as the result of two successive absorptions of λ2537 and that no other radiation is involved. Houtermans showed that the ions are produced probably

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* Now at Lehigh University, Bethlehem, Pennsylvania.

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