THE INFRARED ABSORPTION BANDS OF WATER VAPOR

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Abstract

Further experimental work has been done on the near infrared absorption of water vapor in the regions of 1.40μ and 1.90μ. Forty-five lines have been listed for the region of 1.40μ. There is some difficulty in interpreting this band as to zero branch or double type. By using somewhat higher resolution the 1.87μ band has been shown to consist of more lines than previously observed. The region of 1.87μ has the appearance of a double type band when a small amount of water vapor was used. Calculations have been made as to the form of the water vapor molecule on the assumption that this is the third fundamental band of water vapor. Also, the intensities of the bands have been calculated and these are found to be in good agreement with the experiment values. A new classification has been made of the combination bands.

THE present work gives the results of the absorption of water vapor in the region of 1.40μ and 1.90μ and then a correlation is made with the other bands. The near infrared region has been studied by many observers[1] and each successive work has shown that with higher resolution more lines appeared. Plyler and Sleator[2] have recently made a study of the absorption bands of water vapor in the regions of 1.87μ, 2.67μ, 3.16μ, and 6.26μ, and this work was undertaken to make a study of the fainter bands with high resolution. It was found that the resolution in the band at 1.87μ could be increased and this region was measured again.

The apparatus was the same as that used by Plyler and Sleater[2] and will not be described here. A grating of 15,000 lines was employed in the region of 1.40μ and 1.90μ. The absorbing path was about 6 meters long and the pressure of the water vapor in the air was 2 cm for the absorption bands shown in Fig. 1 and 2, and 1.5 cm for absorption band represented in Fig. 3. The slits were 0.20 mm in width and the wave-length interval included in this slit width has been given in Table I as a function of the resolving power of the instrument.

Table I. *Resolving power of instrument.*

Region	Slit width A	Slit width cm^{-1}
1.40μ	3	1.6
1.90μ	3.5	0.99

[1] E. von Bohr, Phil. Mag. **28**, 71 (1914); G. Hettner, Ann. d. Physik **55**, 476 (1918); W. W. Sleator and E. R. Phelps, Astrophys. J. **62**, 28 (1925); E. R. McAlister and H. J. Unger, Phys. Rev. **37**, 1012 (1931).

[2] E. K. Plyler and W. W. Sleator, Phys. Rev. **37**, 1493 (1931).

In Fig. 1 a graph has been plotted to show the experimental results for the region of 1.40μ. The galvanometer deflections in mm have been plotted as the ordinate and the angle of the grating has been plotted as the abscissa. A large number of lines were found for this region.

TABLE II. *Region of 1.40μ. Intensity, wave-number and wave-length of lines.*

Line No.	Wave-length	Wave number	Rel. Int.	Line No.	Wave-length	Wave number	Rel. Int.
1	13461	7428.9	5	24	13767	7263.7	15
2	13474	7421.5	10	25	13783	7255.2	20
3	13484	7416.4	10	26	13803	7244.7	45
4	13499	7407.8	10	27	13824	7234.0	55
5	13519	7396.7	5	28	13833	7229.3	30
6	13526	7393.0	8	29	13846	7222.2	15
7	13545	7383.2	18	30	13853	7218.7	12
8	13554	7378.2	20	31	13868	7210.8	40
9	13572	7368.3	8	32	13901	7194.0	5
10	13583	7362.2	10	33	13920	7184.2	40
11	13590	7358.2	15	34	13950	7168.3	40
12	13603	7351.0	10	35	13959	7164.3	45
13	13619	7342.8	50	36	13968	7159.3	15
14	13643	7330.0	30	37	14001	7142.3	50
15	13649	7326.7	40	38	14008	7138.5	30
16	13664	7318.7	10	39	14053	7120.5	40
17	13673	7313.8	25	40	14069	7108.2	30
18	13682	7309.0	30	41	14093	7095.8	30
19	13693	7302.7	8	42	14142	7071.2	25
20	13704	7297.0	20	43	14171	7056.5	10
21	13717	7290.3	25	44	14189	7047.7	15
22	13743	7276.2	10	45	14233	7025.6	15
23	13754	7270.7	10				

In Table II the line number, intensity, wave number and wave-length for 45 of the more intense lines are listed. The values given in this table were obtained by taking the average values from two different curves. It was found that the wave-lengths of the two curves never varied over 2A for any line. This band has a region of about 40 waves per cm which has very little absorption. This is the spacing between the strong lines of the 6.26μ band and would indicate that this band is of the double type with its center at 13750A. This band is the first harmonic of the zero branch type band at 2.67μ and it would be expected to be also of the zero type. However, a change in the type of band from fundamental to harmonic has been observed in certain cases. If this band is of the zero branch type its center is probably located at 13840A.

The region of 1.90μ has been studied and the results obtained are given in Fig. 2 and Table III. The resolution used is somewhat greater than in the work of Plyler and Sleator[2] and has made it possible to separate some lines which formerly appeared as one. The curve given in this paper shows the lines as sharper and the intensities are probably more accurately represented. There are listed 68 of the more intense lines in Table III. Many of the wave-lengths check closely with the values found in the previous study, but in the first 25 lines the wave-lengths given in this paper are about 6A greater. It is believed that the values given here are more reliable than those in the previous paper and should replace them.

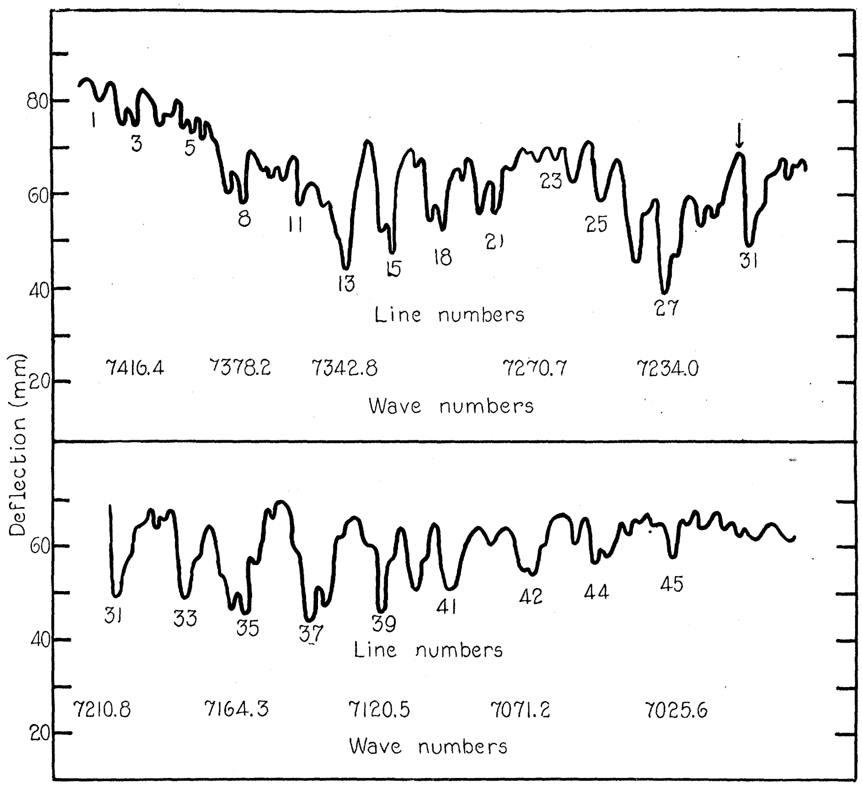

Fig. 1. Energy curve for the region of 1.40μ. Slit width 3A.

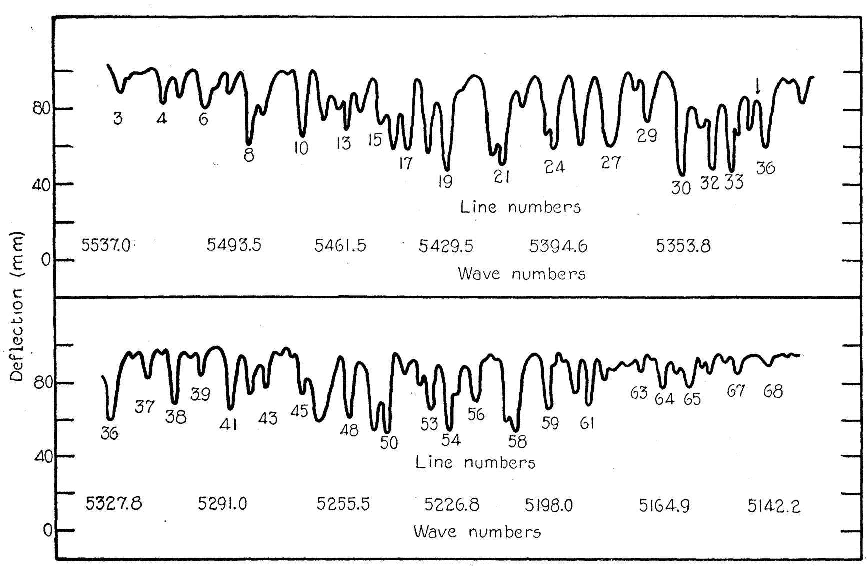

Fig. 2. Energy curve for region of 1.90μ. Slit width 3.5A.

TABLE III. *Region of 1.90μ. Intensity, wave number and wave-length of lines.*

Line No.	Wave-length	Wave number	Rel. Int.	Line No.	Wave-length	Wave number	Rel. Int.
1	18006	5553.3	5	35	18750	5333.4	20
2	18023	5549.4	5	36	18770	5327.8	40
3	18060	5537.0	10	37	18812	5315.8	15
4	18104	5523.6	15	38	18838	5308.3	20
5	18126	5517.0	12	39	18853	5304.2	10
6	18152	5509.0	20	40	18866	5300.6	15
7	18180	5500.6	10	41	18900	5291.0	40
8	18203	5493.5	45	42	18920	5285.4	25
9	18220	5488.5	20	43	18935	5281.2	15
10	18261	5476.1	40	44	18964	5273.2	10
11	18285	5467.7	25	45	18977	5269.6	15
12	18302	5463.9	15	46	18993	5265.4	45
13	18310	5461.5	25	47	19004	5262.0	10
14	18325	5457.0	15	48	19028	5255.5	40
15	18345	5451.0	25	49	19052	5248.8	45
16	18362	5446.0	40	50	19064	5245.7	45
17	18375	5442.1	40	51	19087	5240.0	15
18	18399	5435.1	40	52	19102	5235.0	15
19	18418	5429.5	50	53	19112	5232.3	40
20	18469	5414.5	45	54	19132	5226.8	45
21	18480	5411.3	45	55	19142	5224.1	20
22	18502	5404.8	15	56	19160	5219.1	30
23	18530	5396.7	20	57	19196	5209.4	40
24	18537	5394.6	40	58	19205	5207.0	45
25	18564	5386.2	40	59	19238	5198.0	35
26	18597	5377.4	50	60	19267	5190.2	20
27	18604	5375.5	35	61	19283	5186.0	25
28	18629	5368.0	10	62	19302	5180.8	15
29	18641	5364.5	25	63	19338	5171.1	10
30	18679	5353.8	60	64	19362	5164.9	15
31	18695	5349.0	20	65	19380	5159.9	15
32	18708	5345.3	50	66	19392	5156.8	10
33	18727	5339.8	50	67	19413	5151.4	10
34	18735	5337.6	15	68	19448	5142.2	5

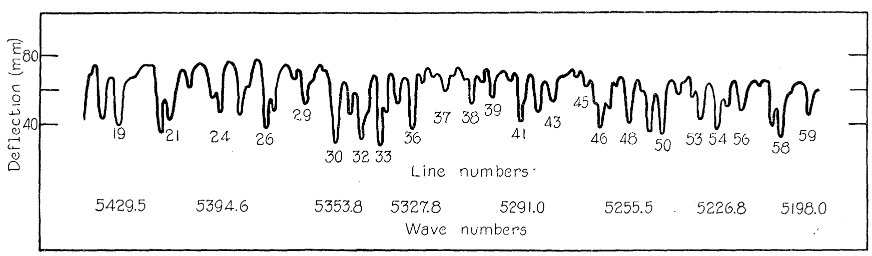

Fig. 3. Energy curve for region of 1.88μ with less water vapor present. Slit width 3.5A.

The part of this band at 1.8865μ appeared to have very few strong lines and it was studied again with less water vapor (1.5 cm pressure). It was found that the region then appeared more definitely as a separate band. The spacing between the two strong lines, numbers 36 and 41, is 37 waves per cm, which is of the order of that for the 6.26μ and 3.16μ bands, the spacing for the former band being 40 waves per cm and the latter 45 waves per cm. Lines number 41, 42, 43 on the longer wave-length side and numbers 34, 35 and 36 on the shorter wave-length side have very much the same appearance as the first three lines on each side of the center as found in the 6.26μ band. This region is overlapped by the combination band $\nu_1+\nu_2$ and it is not possible to make a very complete correlation of lines, but the longer wave-length side has its stronger lines a considerable number of waves per cm from the center, as in the 6.26μ band. If this is a separate band overlapping the combination band at 1.87μ, it is probably the third fundamental band of water vapor. So far only the bands in the regions of 2.67μ and 6.26μ have been classified as fundamental bands.

By using the values of 5309, 1597, 3742 waves per cm as the fundamental frequencies of water vapor, the angle that the oxygen atom makes with the hydrogen atoms has been calculated by the use of the equation derived by Dennison.[3] The value obtained is 115° or the half angle, $\alpha=57.5°$. Also, the intensities have been calculated and found to be of the right order of magnitude. In Table IV are given the calculated and experimental intensities. The intensity of the 6.26μ band is set equal to 100 in the two cases by choosing the proper constants. It is difficult to determine the true intensity of a band and the experimental values should be considered as approximate.

TABLE IV. *Intensity of bands.*

Band	Frequency in waves per cm	Observed intensity	Calculated intensity
ν_1	3742	75	78.4
ν_2	1597	100	100
ν_3	5309	10	6.7

Also, if we consider 5309 waves per cm as the third fundamental of water vapor a complete classification of the near infrared bands of water vapor can be made. The theoretical frequency of the bands cannot be calculated for there is not known the correct frequency of a sufficient number of combination bands to determine the correction terms. However, the calculated frequency has been given in Table V without the correction terms to show that the assigned combinations are of the right order of magnitude.

TABLE V. *Combination bands. Calculated and observed values.*

Combination term	Experimental frequency	Calculated frequency
ν_1	3742	3742
ν_2	1597	1597
ν_3	5309	5309
$\nu_1+\nu_2$	5343	5339
$\nu_1+\nu_3$	8848	9095
$\nu_2+\nu_3$	6896	6906
$2\nu_1$	7224	7448
$2\nu_2$	3156	3194
$\nu_1+\nu_2+\nu_3$	10638	10648
$2\nu_3$		10618

[3] D. M. Dennison, Phil. Mag. **1**, 195 (1926).

The combination bands are given different designations from those given by Hettner.[4] The frequencies obtained by the present arrangement do not check better than those in Hettner's arrangement, but it is believed that the intensities of the observed bands may be more in accord with the probable intensities in the present combinations.

The experimental work of this paper was done in the Physical Laboratory of the University of Michigan and the writer wishes to express his appreciation to Professors Meyer and Barker for the use of their equipment.

[4] G. Hettner, Zeits. f. Physik **1**, 345 (1920).