FURTHER STUDY OF THE ABSORPTION OF INFRARED RADIATION BY WATER VAPOR

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(Received April 8, 1931)

Abstract[1]

Making use of a spectrometer with a salt prism and echelette gratings, and a Moll thermal relay, the authors have reexamined with increased resolution the four absorption bands of water vapor whose centers lie near 1.87μ, 2.66μ, 3.15μ and 6.26μ. The new study has greatly increased the number of measured lines. Near 6.26μ and 3.17μ the number has been more than doubled. The new lines are mostly weak ones, but the work has resulted in a better determination of the wave-lengths of many strong lines, which now appear as sharp single effects freed from the former confusion in which several lines were taken for one. The center of the harmonic of the band at 6.26μ is seen to be better placed at 3.168μ than it was formerly at 3.11μ. It also appears that this band has no absorption at the center, and is of the same type as the fundamental.

Introduction

THE work to be described in this paper was done at the University of Michigan during the summers of 1928, and 1929, and the fall of 1930. It was found, after working over the atmospheric absorption near 2.66μ, that the apparatus now available, because of the higher resolution of which it is capable, permitted a more precise and complete analysis of the absorption spectrum of water than had been given in the papers by Sleator[2] and Sleator and Phelps.[3] A real advance may be claimed when what was formerly considered to be, and measured as, a single line, proves, as the present work in many cases shows, to consist of three or four. Furthermore many of the lines now given in the charts and tables are very sharp, and many more lines show in these figures quite the same shape, and this indicates that they are single effects, and not likely to break up on more refined analysis. On account of this better identification, and on account of more accurate calibration now employed, there is reason to think that the wave-lengths here given are more precise than the earlier numbers, which they should supplant.

Of the bands here studied, those near 6.26μ and 2.66μ have been classified as fundamentals, with vibration frequencies ν_1 and ν_2 respectively, the latter having a zero branch, the former being double. The frequency at 1.87μ represents the combination $\nu_1+\nu_2$ and that at 3.16μ is $2\nu_1$, so that this band is the first harmonic of that at 6.26μ. A classification of the known absorption bands of water has been given by Hettner.[4]

[1] This abstract appeared in the Bulletin of the American Physical Society of November 15, 1930, announcing the Chicago Meeting.

[2] W. W. Sleator, Astrophys. J. **48**, 125 (1918). References to earlier work are given in this paper.

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

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

Experimental Procedure

The apparatus used was the compound spectrometer with sodium chloride prism and grating in series, of the type commonly used for work in the infrared, constructed and described by Meyer.[5] The grating used for the band at 6.26μ had 2,880 lines per inch, that employed for the others had 7,200. They were ruled by Barker. The thermopile was constructed and has been described by Firestone.[6] By adjusting the lamp which illuminates the thermocouple in the Moll relay the amplification factor could be controlled, and could be brought up to 300 by using a current of 3.5 amperes. At this amplification Brownian motion could be observed, so that four or six, sometimes eight, independent deflections of the galvanometer were taken at each setting of the grating. Small vibrations of the building due to the wind and other things affected the galvanometer. It was necessary to take most of the readings at night.

The spectrometer circle was set at a certain angle, then the deflections were read, then the circle was turned 15 seconds, and deflections taken again. This was continued through the region—that at 6.26μ extended over about 6 degrees. The graph which revealed the absorption lines was plotted with average deflection as ordinate, and angle or wave number as abscissa. The determination of the wave-length of a line depends in most cases upon three independent energy curves—in some cases more.

The step by which the circle was advanced between successive galvanometer readings was less than the angular value of the slit itself. In Table I, the data of which are given separately with the different figures, the degree of resolution used in the different bands is shown by giving the wave-length interval included in the second slit. Values used by Sleator and Phelps are shown for comparison.

TABLE I. *Effective resolving power.*

Region	Slit width (A.U.)	Slit width (cm^{-1})	Slit width (Sleator and Phelps) (A.U.)
1.87μ	4.1	1.16	8
2.66μ	3.1	0.44	
3.15μ	4.5	0.45	32
6.26μ	17.	0.45	80

The observations in this work were made upon the absorption by the water vapor in the air of the room. For the bands at 1.87μ and 3.16μ the absorption did not anywhere exceed forty percent, and it was not necessary to remove any moisture. In the other bands, however, there were very strong lines which could not be separated. In order to reduce the amount of water present a rough box was built around the spectrometer and phosphorus pentoxide was exposed inside. The effect of such drying is shown, for example, by the

[5] Aaron Levin and Charles F. Meyer, J.O.S.A. and R.S.I. **16,** 137 (1928).

[6] F. A. Firestone, Rev. Sci. Inst. **1,** 630 (1930).

inserted sections near line No. 177 in the curve of Fig. 5. Drying the air made it possible to separate and identify the lines. The pressure of water vapor in the undried air was 20 to 30 mm. In the dried air it was 2 to 3 mm. Fig. 3 also represents the energy curve near 2.66μ with dried air. Lines nos. 22, 23 and 24, for example, are better defined in this figure than in Fig. 2, which refers to the normal indoor atmosphere.

Results and Discussion

The measurements made during this work appear in the curves of the following figures, and in the tables. The tables show an arbitrary number for each line, and its relative intensity, wave-length, and wave-number. The relative intensities represent estimates only, based upon the depth of the lines. In many cases this estimate has been difficult and uncertain, because a certain line may represent only a weak absorption upon the side, so to speak, of a deeper and wider line, or it may represent a stronger effect if its neighbor is in fact a weaker one. Line number 35 in Figure 3, for example, has been assigned a relative intensity of 50 percent. But if it is really only a nick in the curve which shows No. 36 it ought to be marked, perhaps, 15 percent. In all cases where two lines over-lap there is doubt about the intensity of each. This composite effect, which partly disappeared when the air was dried, made it impossible to use the criterion of the area of the notch for estimating intensity. Improvement of the present analysis of the water spectrum demands first of all an enclosed spectrometer and absolute control of the amount of the absorbing medium. Second, it demands a resolution even higher than we could command.

When the amount of moisture was reduced by the means described, many lines in all the bands were made more narrow and sharp. On advancing the circle 15 seconds, the galvanometer deflection changed in may cases by 40 mm—say from 100 to 60. An error of 5 seconds in setting might affect the deflection by 15 mm. This unavoidable uncertainty of perhaps 5 seconds in setting may account for the difference in relative intensities of two lines as they appear in different curves, so that in one graph a is stronger than b, in another not so strong.

Figure 1 and Table II represent our study of the band at 1.87μ. Many new lines have appeared, for example line No. 48 in Fig. 5 of the paper of 1925 seems now to be a composite effect of those numbered 81, 82, and 83. There is no way of deciding what wave length, with the amount of water uncontrolled, such a combination ought to have. Accordingly there is no satisfactory basis for comparison of wave-lengths. In general, however, the new values are larger.

It may be remarked here that the numbers assigned to the lines are arbitrary. Also we have omitted numbers from all the tables at places where there are faint lines of uncertain positions, to which we cannot assign definite wave lengths.

In work done at Johns Hopkins University by Barnes[7] the energy of a

[7] R. Bowling Barnes, Phys. Rev. **36**, 296 (1930).

source of radiation was mapped in the region between 3 and 4μ. It shows two bands of atmospheric absorption, one of them with center near 3.73μ. With

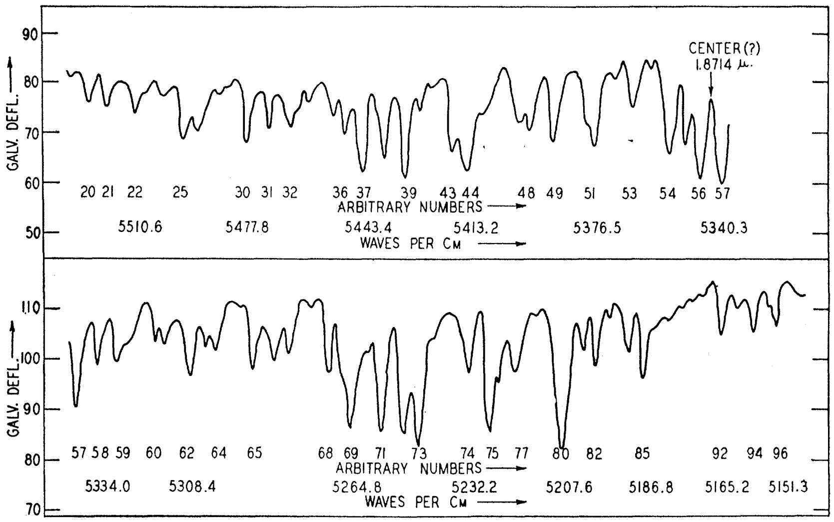

Fig. 1. Energy curve, region of 1.87μ, middle part. Echelette grating, 7200 lines per inch. Slits 0.12 mm, 12.4 secs, 1.16 waves per cm, 4.1A.

TABLE II. *Region of* 1.87μ.
Arbitrary numbers, relative intensities, wave-lengths, and wave-numbers of the stronger lines.

Line No.	Rel. int.	Wave-length	Wave-number	Line No.	Rel. int.	Wave-length	Wave-number
20	10	18100	5524.9	57	35	18725	5340.5
21	10	18117	5519.7	58	20	18747	5334.2
22	10	18146	5510.8	59	20	18769	5327.9
24	5	18174	5502.4	60	10	18801	5318.9
25	15	18194	5496.3	61	10	18811	5316.0
26	15	18209	5491.8	62	15	18837	5308.7
28	5	18229	5485.8	63	10	18851	5304.8
30	15	18255	5477.9	64	10	18865	5300.8
31	10	18278	5471.1	65	15	18900	5291.0
32	10	18300	5464.5	66	15	18920	5285.4
34	5	18318	5459.1	67	15	18934	5281.5
35	10	18342	5452.0	68	15	18974	5270.4
36	10	18352	5449.0	69	25	18994	5264.8
37	25	18370	5443.7	71	25	19025	5256.2
38	20	18392	5437.1	72	25	19048	5249.9
39	25	18412	5431.2	73	30	19063	5245.8
40	5	18428	5426.5	74	15	19112	5232.3
43	15	18459	5417.4	75	25	19132	5226.8
44	25	18473	5413.3	77	15	19158	5219.8
47	10	18525	5398.1	80	30	19202	5207.8
48	15	18535	5395.2	81	10	19225	5201.5
49	20	18557	5388.8	82	15	19235	5198.9
51	25	18599	5376.6	84	10	19269	5189.7
53	15	18636	5366.0	85	15	19279	5187.0
54	30	18672	5355.6	92	10	19360	5165.3
55	25	18688	5351.0	94	10	19391	5157.0
56	30	18703	5346.7	96	10	19412	5151.5

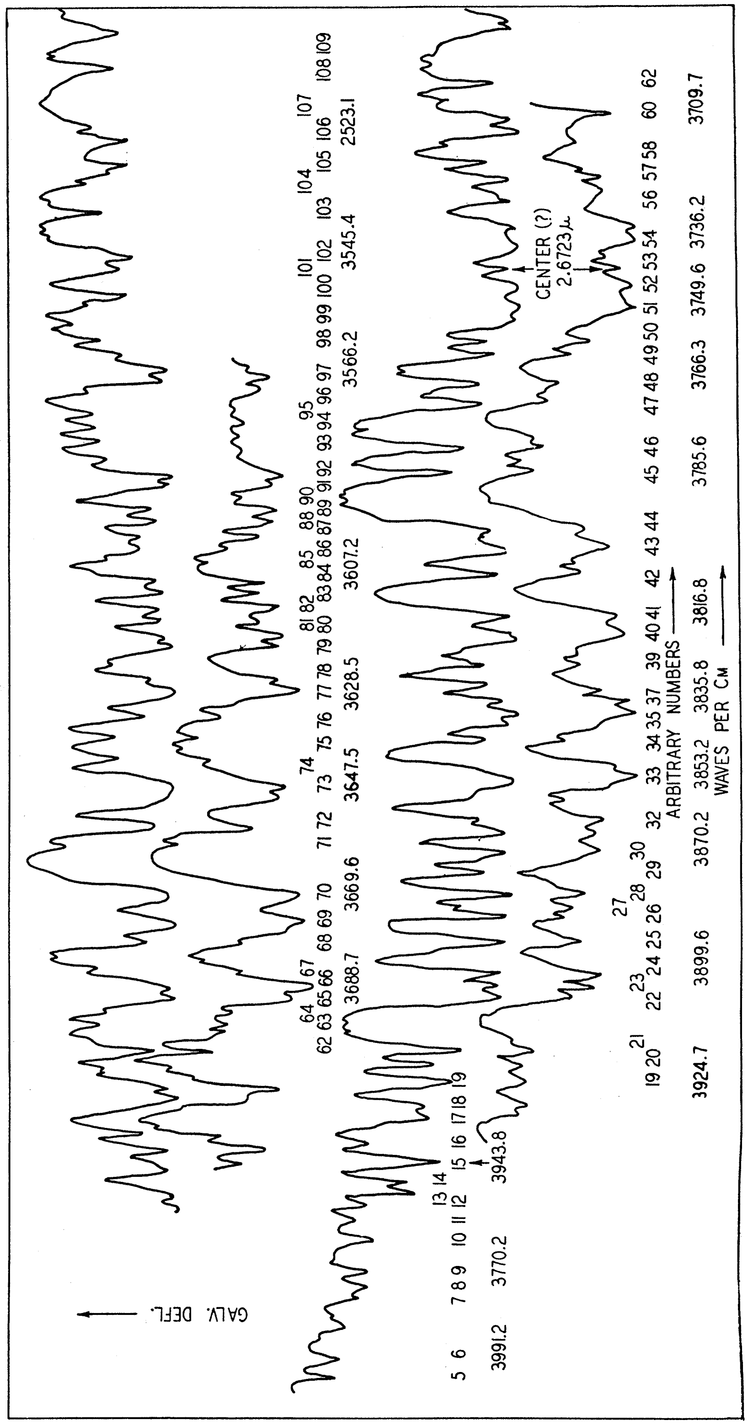

Fig. 2. Part of the energy curve, region of 2.66μ, two independent series. Echelette grating, 7200 lines per inch. Slits 0.1 mm, 10 secs, 0.44 waves per cm, 3.1A.

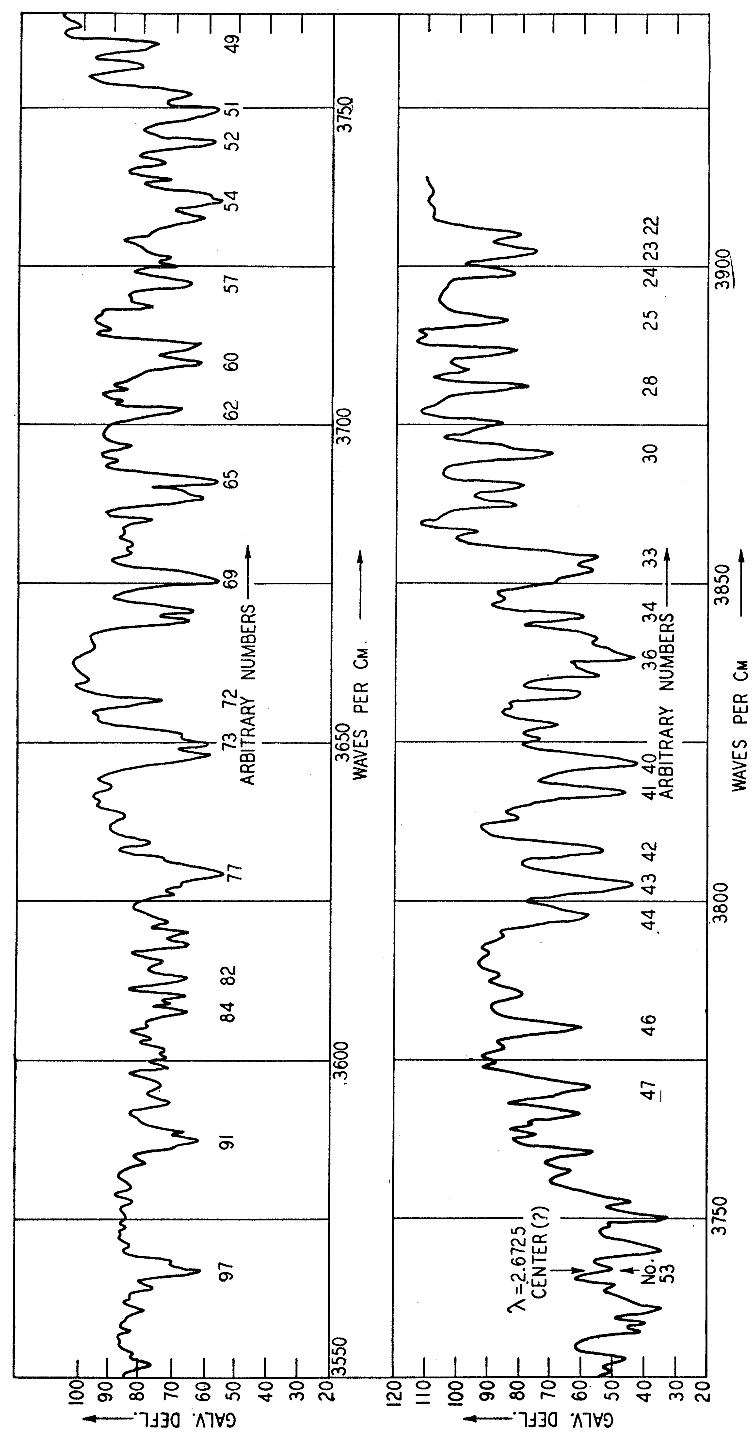

Fig. 3. Energy curve, part of the region of 2.67μ, on frequency scale. Air partly dried. Echelette grating, as in Fig. 2.

the prism-grating spectrograph we have carefully gone over part of this region, having the prism so placed that there was no deflection when the grating was set for 1.9μ. No absorption lines were to be found, though the slits were certainly narrow enough to show them. If certain wave-lengths given in Table II, beginning with No. 26, are multiplied by 2, the products agree remarkably well with many of the wave-lengths given by Barnes. Some of his numbers represent a good mean of adjacent wave-lengths, doubled. For example for line No. 26, 2λ is 3.6418μ. Barnes lists 3.642. Also if one compares the graph under consideration with that for the region near 1.87μ given in Fig. 4 of the paper of 1918 (reference 2) they appear very much alike. The work of Barnes was done with a grating and an infrared filter. It may be that the atmospheric absorption appearing at 3.75μ in Figs. 4 and 5 of that paper is a second order effect due to an overlapping of spectra.

In Figs. 2 and 3 and Table III are given our results for the region of 2.67μ, a fundamental band having a zero branch—showing at any rate strong absorption in the middle portion. Of the two curves in Figure 2 there is less moisture represented in the lower. For Fig. 3 there is less vapor still, and there is less overlapping and general confusion of the lines. For example, line No. 70

TABLE III. *Region of* 2.67μ.
Arbitrary numbers, relative intensities, wave-lengths and wave-numbers of the stronger lines.

Line No.	Rel. int.	Wave-length	Wave-number	Line No.	Rel. int.	Wave-length	Wave-number
1	15	24714	4046.3	29	60	25806	3875.1
1a	5	24795	4033.1	30	80	25838	3870.3
2	10	24834	4026.7	31	70	25869	3865.6
3	6	24871	4020.7	32	20	25892	3862.2
3a	5	24924	4012.2	33	80	25948	3853.9
4	10	24942	4009.3	33a	80	25959	3852.2
5	12	25027	3995.7	34	40	26010	3844.7
6	12	25055	3991.2	35	50	26031	3841.6
7	8	25103	3983.6	36	80	26049	3838.9
7a	6	25147	3976.6	37	20	26070	3835.8
8	12	25155	3975.4	38	50	26090	3832.9
9	12	25187	3970.3	39	40	26124	3827.9
10	15	25235	3962.8	40	85	26166	3821.8
11	6	25256	3959.5	41	80	26198	3817.1
12	10	25289	3954.3	42	75	26261	3807.9
13	30	25309	3951.2	43	85	26298	3802.6
14	20	25327	3948.4	44	55	26332	3797.7
15	40	25356	3943.8	45	55	26415	3785.7
16	12	25379	3940.3	46	60	26454	3780.1
17	40	25427	3932.8	46a	5	26493	3774.6
18	20	25442	3930.5	47	70	26521	3770.6
19	5	25479	3924.8	48	70	26550	3766.5
20	40	25506	3920.7	48a	10	26570	3763.6
21	55	25527	3917.4	49	75	26594	3760.2
22	50	25610	3904.7	50	50	26612	3757.7
23	65	25624	3902.6	50a	20	26647	3752.8
24	65	25644	3899.5	51	85	26667	3749.9
25	70	25694	3892.0	52	85	26700	3745.3
26	60	25731	3886.4	53	60	26724	3742.0
27	10	25746	3884.1	53a	20	26746	3738.9
28	70	25766	3881.1	54	85	26762	3736.6

TABLE III. (*Cont'd.*)

Line No.	Rel. int.	Wave-length	Wave-number	Line No.	Rel. int.	Wave-length	Wave-number
55	85	26790	3732.7	81	50	27660	3615.3
56	80	26825	3727.9	82	60	27679	3612.8
57	80	26863	3722.6	83	40	27700	3610.1
58	50	26889	3719.0	84	40	27720	3607.5
58a	20	26915	3715.4	85	10	27757	3602.7
59	80	26936	3712.5	86	30	27771	3600.9
60	80	26954	3710.0	87	30	27789	3598.6
61	30	26982	3706.2	88	40	27810	3595.8
62	60	27011	3702.2	89	30	27828	3593.5
63	25	27051	3696.7	90	30	27867	3588.5
64	15	27068	3694.4	91	65	27875	3587.4
65	80	27092	3691.1	92	20	27902	3584.0
66	85	27109	3688.8	93	20	27932	3580.1
67	10	27135	3685.3	94	20	27951	3577.7
68	10	27175	3679.9	95	20	27977	3574.4
69	80	27208	3675.4	96	10	28003	3571.0
70	80	27241	3670.9	97	70	28036	3566.8
70a	40	27251	3669.6	97a	20	28056	3564.3
71	10	27320	3660.3	98	20	28085	3560.6
72	70	27349	3656.4	99	15	28110	3557.5
72a	80	27398	3649.9	100	30	28151	3552.3
73	60	27415	3647.6	101	30	28188	3547.6
74	20	27452	3642.7	102	30	28204	3545.6
75	30	27486	3638.2	103	25	28276	3536.6
76	50	27517	3634.1	104	10	28320	3531.1
77	80	27557	3628.8	105	30	28348	3527.6
78	20	27575	3626.5	106	30	28384	3523.1
78a	30	27608	3622.1	107	10	28406	3520.4
79	60	27626	3619.8	108	30	28493	3509.6
80	40	27640	3618.0	109	30	28546	3503.1

is separated in Fig. 3, into two lines some 10A apart. Further comparison shows that the intensity of all the strong lines increases with the amount of water present. This change in intensity indicates that at least the strong lines in this region are due to water vapor, and not to carbon dioxide. The carbon dioxide band in the region of 2.73μ would probably not have strong lines below 2.69μ, corresponding to line No. 59. The effect of carbon dioxide in this region was studied by Sleator[2] and it was found that the strong lines throughout the region were enhanced by the use of steam (giving much more absorbing material) and reduced by drying the air. Figure 3 has been plotted with deflections on a scale of frequencies and is the reverse of the curves of Figure 2. Lines 22, 23 and 24 may be compared with the unresolved group shown as numbers 8 and 9 in Figure 5 of the paper of 1918, and this comparison fairly indicates the advance represented in the present work.

In Fig. 4 and Table IV are represented the results for the region of 3.16μ. It is perhaps here that previously published results are most inadequate. The table presents lines between 2.85 and 3.33μ, and the lines at the beginning of the table probably belong to the series shown in the previous figures. All the lines are weak in this region, whose center we have placed at 3.168μ, and which is probably the first harmonic of the band at 6.26μ. However, the separation of the two strong lines next the center on either side (Nos. 81 and 82) is 45.3 waves per cm, while the corresponding difference at the fundamental

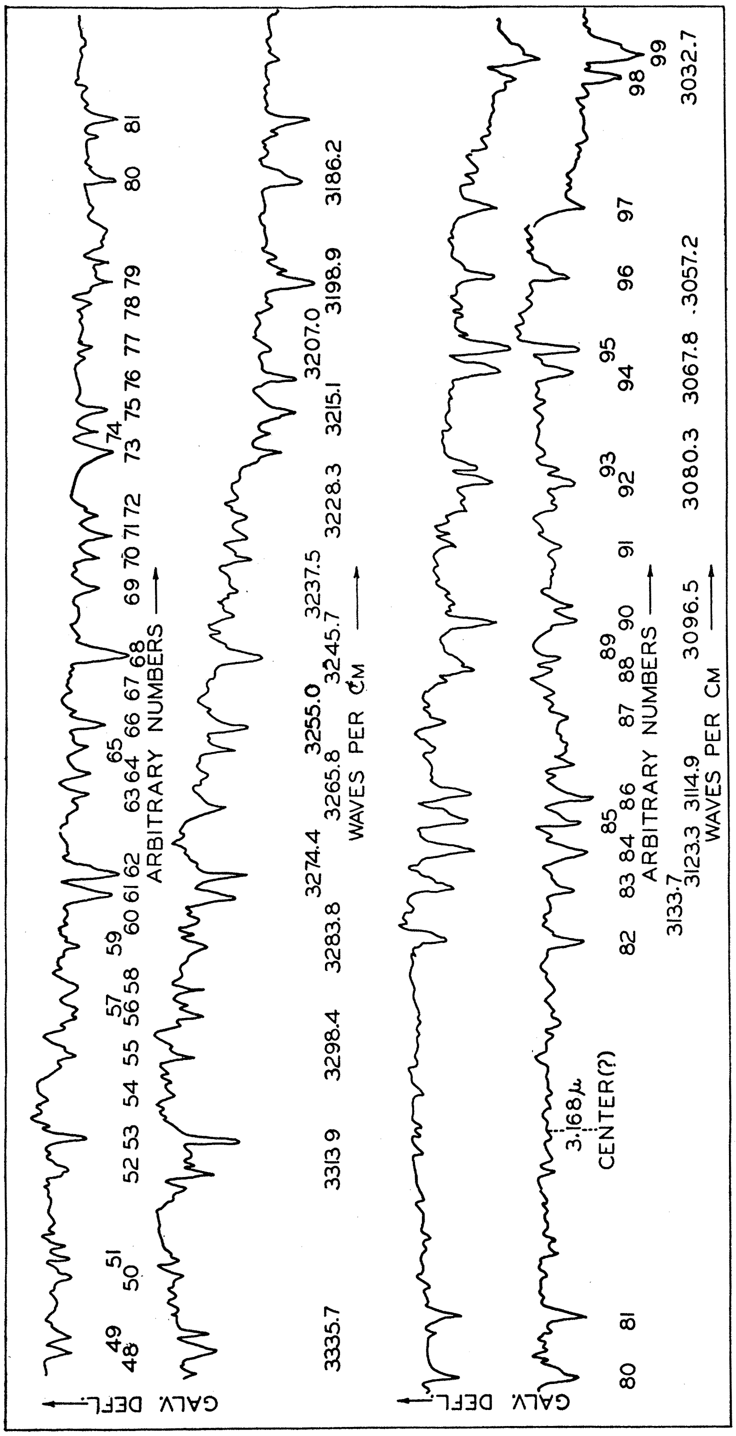

Fig. 4. Part of the energy curve, region of 3.16μ. Two independent series. Echelette grating, 7200 lines per inch. Slits 0.15 mm, 15 secs, 0.45 waves per cm, 4.5A.

TABLE IV. *Region of* 3.15μ
Arbitrary numbers, relative intensities, wave-lengths and wave-numbers of the stronger lines.

Line No.	Rel. int.	Wave-length	Wave-number	Line No.	Rel. int.	Wave-length	Wave-number
1	40	28546	3503.1	59	12	30452	3283.9
2	5	28561	3501.3	60	5	30489	3279.9
3	15	28588	3498.0	61	25	30515	3277.1
4	25	28655	3489.8	62	25	30540	3274.4
5	12	28672	3487.7	63	8	30620	3265.8
6	25	28702	3484.1	64	8	30663	3261.3
7	25	28714	3482.6	65	8	30693	3258.1
8	15	28762	3476.8	66	12	30721	3255.1
9	5	28801	3472.1	67	5	30762	3250.8
10	15	28828	3468.9	68	20	30809	3245.8
11	5	28844	3466.9	69	12	30887	3237.6
12	15	28861	3464.9	70	10	30923	3233.8
13	15	28873	3463.4	71	15	30949	3231.1
14	5	28901	3460.1	72	15	30976	3228.3
15	5	28919	3457.9	73	25	31053	3220.3
18	35	28992	3449.2	74	8	31077	3217.9
19	5	29013	3446.7	75	25	31102	3215.2
20	20	29032	3444.5	76	20	31144	3210.9
22	8	29066	3440.4	77	5	31181	3207.1
26	15	29128	3433.1	78	5	31237	3201.3
27	5	29161	3429.2	79	20	31261	3198.9
28	8	29176	3427.5	80	15	31384	3186.3
29	5	29194	3425.4	81	20	31456	3179.0
30	12	29206	3424.0	82	20	31911	3133.7
31	30	29219	3422.4	83	20	31972	3127.7
32	5	29265	3417.1	84	25	32017	3123.3
33	10	29318	3410.9	85	12	32054	3119.7
34	12	29366	3405.3	86	25	32103	3115.0
37	12	29437	3397.1	87	10	32176	3107.9
39	15	29457	3394.8	88	15	32239	3101.8
42	12	29528	3386.6	89	12	32256	3100.2
43	5	29687	3368.5	90	20	32294	3096.5
44	12	29703	3366.7	91	5	32385	3087.8
45	8	29736	3362.9	92	12	32463	3080.4
46	12	29789	3356.9	93	8	32480	3078.8
47	5	29880	3346.7	94	25	32596	3067.9
48	15	29961	3337.6	95	25	32623	3065.3
49	12	29979	3335.7	96	20	32710	3057.2
50	8	30050	3327.8	97	25	32791	3049.6
52	12	30175	3314.0	98	20	32948	3035.1
53	15	30218	3309.3	99	25	32973	3032.8
54	4	30269	3303.7	100	5	32984	3031.8
55	15	30317	3298.5	101	5	33039	3026.7
56	12	30366	3293.2	102	12	33135	3018.0
57	15	30377	3292.0	103	12	33192	3012.8
58	15	30401	3289.4				

is 40. The wave-lengths of certain lines listed in Table IV are in good agreement with values given by Barnes in the work cited (reference 7) for this region. In some cases his numbers represent averages of the wave-lengths of adjacent lines.

The results for the fundamental at 6.26μ are shown in part in Figs. 5 and 6, and completely in Table V. Hettner shows this band to extend from 4.5μ to 8.5μ, but we have studied only the central part. In Fig. 6 are represented the most important lines of this region on a scale of wave-numbers, showing by the length of the lines the intensities of absorption. The advancement lately

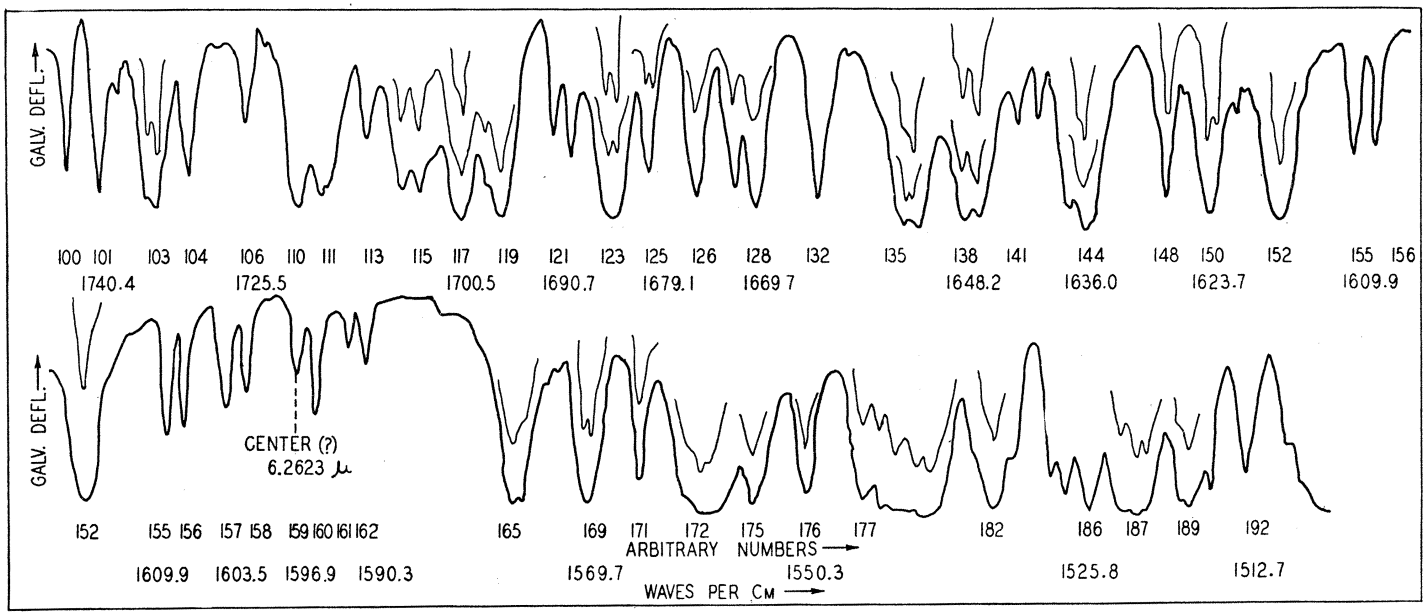

Fig. 5. Energy curve, region of 6.26μ, middle part. Echelette grating, 2880 lines per inch. Slits 0.2 mm, 21 secs, 0.45 waves per cm, 17A.

TABLE V. *Region of* 6.26μ.
Arbitrary numbers, relative intensities, wave-lengths, and wave-numbers of the stronger lines.

Line No.	Rel. int.	Wave-length	Wave-number	Line No.	Rel. int.	Wave-length	Wave-number
58	20	54413	1837.8	144	90	61128	1635.9
63	60	54644	1830.0	148	70	61414	1628.3
65	10	54673	1829.1	149	80	61570	1624.2
66	40	54774	1825.7	150	40	61602	1623.3
67	10	54839	1823.5	152	90	61841	1617.0
69	10	55005	1818.0	155	50	62117	1609.9
70	10	55159	1812.9	156	40	62202	1607.7
71	30	55211	1811.2	157	40	62358	1603.6
72	15	55288	1808.7	158	35	62435	1601.7
73	5	55385	1805.5	159	30	62625	1596.8
76	10	55487	1802.2	160	45	62693	1595.1
77	50	55541	1800.5	161	20	62804	1592.3
78	30	55661	1796.6	162	30	62880	1590.3
79	65	55762	1793.3	165	90	63425	1576.7
80	65	55814	1791.7	168	75	63693	1570.0
81	25	56004	1785.6	169	80	63706	1569.7
82	60	56142	1781.2	171	60	63884	1565.3
83	15	56184	1779.9	172	90	64115	1559.7
84	30	56295	1776.4	173	80	64142	1559.0
85	20	56396	1773.2	175	80	64321	1554.7
86	70	56439	1771.8	176	80	64500	1550.4
87	50	56533	1768.9	177	70	64706	1545.5
89	50	56739	1762.4	178	70	64765	1544.0
90	5	56832	1759.6	179	80	64833	1542.4
91	50	56898	1757.5	180	80	64916	1540.5
93	70	57082	1751.9	181	85	64960	1539.4
95	75	57169	1749.2	182	90	65193	1533.9
97	25	57219	1747.7	183	30	65261	1532.3
98	20	57250	1746.7	184	20	65396	1529.1
100	50	57338	1744.0	185	70	65451	1527.9
101	70	57457	1740.4	186	85	65537	1525.9
102	12	57526	1738.3	187	60	65656	1523.1
103	70	57663	1734.2	188	80	65718	1521.7
104	60	57784	1730.6	189	70	65755	1520.8
106	35	57999	1724.2	192	60	65913	1517.1
110	90	58204	1718.1	193	30	65977	1515.7
111	80	58287	1715.6	194	80	66107	1512.7
113	35	58452	1710.8	196	20	66226	1510.0
114	70	58588	1706.8	197	90	66344	1507.3
115	70	58653	1704.9	198	80	66385	1506.4
117	90	58813	1700.3	200	20	66575	1502.1
118	15	58894	1698.0	202	60	66711	1499.0
119	90	58958	1696.1	203	65	66829	1496.4
120	30	59151	1690.6	204	80	67119	1489.9
121	50	59216	1688.7	205	60	67220	1487.7
122	30	59356	1684.8	207	30	67499	1481.5
123	90	59400	1683.5	208	60	67736	1476.3
124	40	59504	1680.6	209	20	67866	1473.5
125	50	59524	1680.0	210	80	67928	1472.1
126	70	59683	1675.5	211	10	68070	1469.1
127	60	59817	1671.8	213	65	68259	1465.0
128	75	59886	1669.8	216	20	68559	1458.6
129	20	59918	1668.9	217	90	68631	1457.1
132	75	60131	1663.0	218	10	68693	1455.8
133	20	60162	1662.2	219	50	68848	1452.5
135	70	60444	1654.4	221	65	69052	1448.2
136	90	60496	1653.0	224	10	69318	1442.6
138	30	60682	1647.9	227	90	69595	1436.9
139	90	60738	1646.4	228	15	69753	1433.6
141	20	60864	1643.0	229	10	69816	1432.3
142	20	60942	1640.9	230	50	69911	1430.4
143	30	61046	1638.1	234	50	70219	1424.1

made is shown definitely in this region. For what appeared in Fig. 2 of the paper of 1925 as uncertain ripples in the level plateau of the center has now become eight very definite lines, numbers 155 to 162, arranged in pairs. The old lines Nos. 69 and 80, the second from the middle region on either side, now appear as two close lines each, Nos. 149 and 150 and Nos. 168 and 169 of Fig. 5. Line 159 which we have marked the center, because it is a geographic mid point, is not a particularly significant line. Some lines separated here, for example, numbers 172 and 173 and 168 and 169, are less than one wave per cm apart.

It may be well to compare some of the wave-lengths with those given in the previous papers from this laboratory. In many cases no basis for comparison exists, for one of the former "lines" now appears as several. However, there are many lines in the region of 2.67μ as it appeared in 1918 which have persisted as single effects, and there are several lines near 1.87μ and 6.26μ

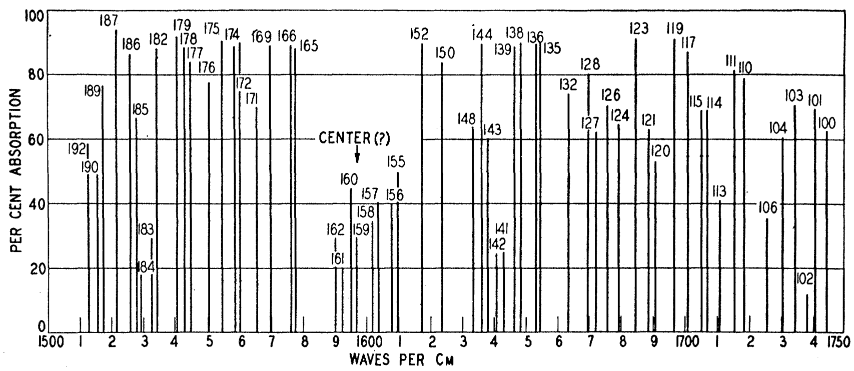

Fig. 6. Region of 6.26μ, middle part. Intensities of the absorption lines shown on a scale of waves per cm.

which may be compared in the paper of 1925 and the present one. The comparison shows that single lines in the band at 2.66μ are now assigned wave lengths from 3 to 7A greater than those of 1918. Perhaps the visual calibration formerly necessary accounts for the systematic difference. Similar differences appear at 1.87μ. At 6.26μ the difference is more irregular and somewhat larger. In many cases, however, no comparison is possible. For example, lines 114 and 115 were formerly given as one, No. 54, and Nos. 120 and 121 as number 58.

Some estimate of the precision attained in the wave lengths listed here is necessary and may be made as follows. The calibration of the 7,200 line grating, used in all the work except for the band at 6.26μ, was based on the mercury line whose wave-length was taken to be 10139.8A in air. This calibration has been done by Meyer, and charts have been made from which wave length and wave number can be read directly in terms of angles. This calibration is believed to involve no error greater than 1 part in 50,000. There exists always some uncertainty in setting the circle. If this amounts to 5 seconds, then the location of an absorption line which depends at the tip upon perhaps four plotted points is also uncertain. Independently measured values of typical lines in two of the regions are shown in Table VI.

TABLE VI. *Typical values for the different angles and wave-lengths found for a single line.*

Line No.	Angle	Wave-length
31	24°31′55″	29219A
	31′55″	29219
	31′55″	29219
	32′0″	29221
33	24°37′25″	29322
	15″	29319
	10″	29317
	15″	29319
39	24°44′42″	29457
	50	29460
	40	29457
	45	29458
128	19°54′22″	59891
	30″	59897
	15″	59885
138	20°10′37″	60672
	45″	60678
	45″	60678
	50″	60682
148	20°26′ 7″	61416
	10″	61418
	5″	61418

When there are extreme differences of 20″ we have taken more than four independent energy curves. It seems fair to affect the values of wave-length in these regions with a probable error of ± 2A. It is perhaps an even chance that the true value of the wave-length in air, based upon the value used here for the mercury line, is within 2A on either side of the values given here. In order to guard against mistakes in reading the calibration charts, values of wave-length and values of wave-number were taken off independently, and afterward checked by looking up all the wave numbers in a table of reciprocals. These considerations and this estimate of precision refer to the regions 1.87μ, 2.66μ and 3.15μ.

The band at 6.26μ was studied with a grating having 2,880 lines per inch. Its calibration was based on the same value of the wave-length of the mercury line at 1μ, and also on work with visual lines. The spectrometer constant was 175,900A. There was no chart available, and our procedure was to compute independent values of λ, one from each plotted curve, by the equation $\lambda = \kappa \sin \theta$. First the wave numbers were looked up in the reciprocal tables, and then the wave numbers were independently computed by using cologs. Typical values in this region are given in Table VI. It does not seem that the spectrometer constant for this assembly is responsible for an error of 1A in our results, and perhaps the wave-lengths in Table V should be written ± 3A. To reduce this uncertainty requires more observations, and more independent curves. The systematic difference between the wave-lengths given here, and those published in the paper of 1925, for such lines as may properly be compared, must arise from differences in calibration constant. The circle used in all this work, as well as in many other investigations made in this laboratory, has no appreciably eccentricity.

The advance over previous work represented here lies, first, in more reliable determinations of individual wave-lengths. Second, more lines have been measured, and this work should make possible a better classification, if it is demanded by theoretical study of the water molecule. Third, the lines measured represent, in more cases than in previous data, single absorption effects, so that more of the wave numbers are of actual physical significance.