The Infra-Red Prism Spectrograph as a Precision Instrument

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An investigation of the working conditions of an infra-red spectrometer of the recording type has resulted in techniques of operation which have increased the precision of the measurements attainable and has permitted an appraisal of the magnitudes of the variations in the resulting data which may still be expected. Included in this study is the remeasurement of the fine structure of certain of the absorption bands of CO_2, NH_3, and H_2O. Measured with a grating instrument whose resolution was made to equal that of the prism instrument in each case, these data give 150 sharp absorption lines between 5μ and 15μ suitable for an empirical calibration of great accuracy.

THAT infra-red spectroscopy has possible solutions for varied types of problems is shown by the fact that many laboratories, both academic and industrial, are adding infra-red spectrographs to their research equipment. With this increased use of infra-red spectroscopy, there comes the desire for increased precision in the results obtained. An extended infra-red spectroscopic investigation made a preliminary study of the operating conditions of a prism recorder both desirable and necessary. While it is recognized that certain of the results given apply only to this particular spectrograph, some of the techniques of operation used are equally applicable to other spectrographs. Also, since the resolution of this spectrograph is roughly the same as that of others now being described[1] and constructed, the calibration data made available here are of general interest.

THE INSTRUMENT

The instrument employed was the infra-red vacuum recording spectrograph described by Randall and Strong.[2] During its twelve years of use, many changes have been made. Figure 1 shows a simplified diagram of the present optical arrangement, the figure being somewhat distorted for clarity. The prism best suited to the region between 5μ and 15μ is of sodium chloride,

the one used here having a refracting angle of 60°, and sides 10 cm long and 8 cm high. The slits are bilateral, the entrance slit being curved sufficiently to make the final image approximately straight. The thermopile is of the type generally used in this laboratory as made by Weyrich, and is best described by Strong.[3] The thermopile and the spectrograph are evacuable separately. All routine adjustments may be made while the case is evacuated. The amplifier used is the one designed by Firestone.[4] This requires a periodic interruption of the optical beam which is accomplished by using a synchronous motor to drive a shutter. The divided circle has been removed, it being established that the Veeder counter, on which a change of one unit indicates a rotation of the prism table through one second of arc, is more reliable than the readings of the circle.

RESOLUTION

The actual resolution of which a spectrograph is capable is best established through a consideration of the fine structure of spectra obtained from the instrument. Thus the $10\text{-}\mu$ band of ammonia, employing a grating spectrograph of the highest resolving power, possesses a fine structure which shows at certain points separations of 3 cm^{-1} between adjacent lines and at other points not far distant, separations of 1.8 cm^{-1}. This prism recorder resolves the lines with the 3-cm^{-1} separations but shows no resolutions

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* Now at The Texas Company, Beacon, New York.

[1] N. Wright, Ind. Eng. Chem. Anal. Ed. **13**, 1 (1941); E. D. McAlister, G. L. Matheson, and W. J. Sweeney, Rev. Sci. Inst. **12**, 314 (1941); W. H. Avery, J. Opt. Soc. Am. **31**, 633 (1941).

[2] H. M. Randall and John Strong, Rev. Sci. Inst. **2**, 585 (1931).

[3] John Strong, *Procedures in Experimental Physics* (Prentice-Hall, 1938), p. 305.

[4] F. A. Firestone, Rev. Sci. Inst. **3**, 163 (1932).

A SOURCE
B SPHERICAL MIRROR
C SHUTTER
D ENTRANCE SLIT
E PLANE MIRROR
F OFF AXIS PARABOLOIDAL MIRROR
G PRISM
H PLANE MIRROR
J PLANE MIRROR
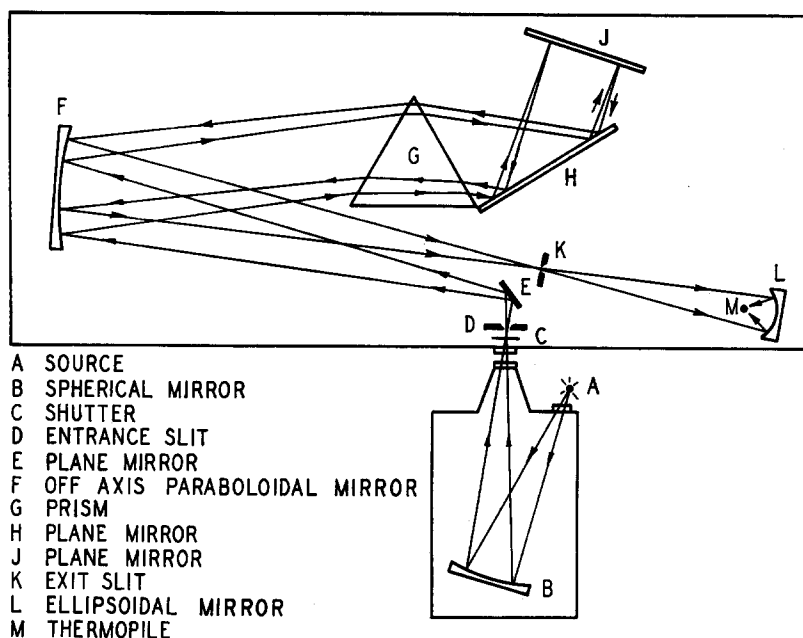K EXIT SLIT
L ELLIPSOIDAL MIRROR
M THERMOPILE

FIG. 1. Schematic diagram of the optical system of the spectrograph.

where the separation is 1.8 cm^{-1}. Judging from recent publications, this represents the maximum resolution being obtained in this spectral region from instruments of this type.

LIMITATIONS IN RECORDING

In seeking to obtain precise data from a spectrograph, it is necessary to investigate several conditions of operation and to determine the limit of accuracy imposed by each of these conditions.

The first condition of operation considered is that of the speed at which the prism is rotated. This must be sufficiently slow so that the response time of the thermopile, the characteristics of the amplifier, and the response time of the recording galvanometer or pen do not cause a displacement of the location of maximum absorption. This may be calculated if sufficient information regarding these parts of the receiving-recording system is available. Or, by operation of the spectrograph at different speeds over absorption bands of varying intensities and widths, the maximum speed may be determined for bands of different types.

Closely associated with this is the fact that

there is a limit to the accuracy with which a recorded spectrum may be read. This is a function of the method of recording and the component parts of the recorder.

It suffices to say that for the spectrograph used in this investigation, if the prism is rotated sufficiently slowly, the center of a sharp absorption line may be determined to within 1 or 2 Veeder counter units.

TEMPERATURE EFFECTS

Although the spectrograph is located in the second basement of the laboratory, extreme temperature variations of 9°C between seasons cause changes in the indices of refraction of the prism material sufficient to shift the spectrum falling on the thermopile by as much as 0.14μ. This is in agreement with the calculations made by Cross.[5] Calculation of the displacement of the spectrum due to temperature changes may be made throughout the spectral region from 1μ to 15μ using the temperature coefficients of the indices of refraction of sodium chloride as assembled from the original investigations by Schaefer and

[5] P. C. Cross, Rev. Sci. Inst. 4, 197 (1933).

Matossi[6] where intermediate values have been added by interpolation. Comparison of the experimental and calculated values shows good agreement at the short-wave end of the spectrum, but poor agreement at the long-wave end. References to the original papers strengthen the expression of Cross,[5] that at least "further determinations of the temperature coefficients would be desirable."

Knowing that temperature effects are appreciable, the ideal solution is to locate the spectrograph where the temperature is maintained constant through a suitable control. An alternative method, and the one used here, is to measure the temperature of the prism and to determine empirically the correction necessary by measuring the effect of temperature changes on known spectral lines throughout the spectrum. For this purpose the positions of the three sharp maxima, 4.225μ of carbon dioxide, 10.073μ of ammonia, and 14.97μ of carbon dioxide were accurately determined with the prism at a number of temperatures covering the range of maximum variation. From these observations it was determined that a temperature change of 1°C in the prism shifted the positions of the 4.225-μ and 10.073-μ lines by 5 Veeder counter units while the position of the 15-μ line was shifted by 4 Veeder counter units. In practice the change from a correction of 5 Veeder counter units per degree to one of 4 Veeder counter units per degree was placed at 13μ. These changes of 5 and 4 Veeder counter units in the positions of these lines correspond to rotations of 5 and 4 seconds of arc, respectively, for the prism. As 22°C is the lowest temperature observed for the prism, all readings at other temperatures are reduced to the equivalent readings at 22°C, and the calibration curve as plotted is correct for this same temperature.

MECHANICAL LIMITATIONS

Imperfections such as might be found in the mechanism for rotating the prism may limit the precision of the spectrograph. Obtaining several spectra of the same absorption line over an interval of time so short that no appreciable change in the temperature of the prism took

place, it was found that differences in the locations of the center of the line amounted to not more than one or two Veeder counter units. Since these are equivalent to the smallest differences that can be read due to the limitations of the method of recording, as indicated in a previous section, it is evident that variations due to mechanical effects over short intervals of time are negligible. To check on possible shifts of the entire spectrum, the 14.97-μ and 4.225-μ maxima of the CO_2 bands were frequently measured with great care; these two are chosen because they are toward the ends of the spectral region, and because atmospheric CO_2 provides a simple means of obtaining them. Over a period of several months, there were no abrupt or erratic shifts in the positions of these lines. However, there was a gradual shift, always in one direction and equal at both ends of the spectrum. As this shift seemed to increase more when the spectrograph was used most, it was attributed to wear. In agreement with this is the fact that no change occurs over extended time intervals if the instrument is idle. Over a period of five months of the most intensive use of this spectrograph, the shift amounted to about 17 Veeder counter units, that is, to 17 seconds of arc rotation of the prism, which corresponds to only a very minute amount of wear when the nature of the driving mechanism is considered.

TABLE I. Data on the position of 4.225-μ line of CO_2.

Date	Prism temp.	Observed position	Corr. for temp.	Shifts	Shift correction
May 12	22.8	89813	89817	−3	
12	25.4	800	817	−3	
12	24.7	803	817	−3	3
12	26.0	797	817	−3	
13	24.7	803	817	−3	
June 12	26.1	793	813	−7	
13	24.8	802	816	−4	
13	26.9	789	814	−6	6
13	27.1	789	815	−5	
14	27.4	787	814	−6	
July 31	30.5	762	805	−15	
31	30.9	760	805	−15	
Aug. 1	30.1	764	805	−15	15
3	30.3	764	806	−14	
7	27.1	778	804	−16	
Aug. 12	29.0	770	805	−15	
13	28.2	772	803	−17	
13	28.3	773	805	−15	16
14	28.2	773	804	−16	
15	27.7	773	802	−18	

[6] C. Schaefer and F. Matossi, *Das Ultrarote Spektrum* (Springer, 1930), p. 47.

The research, of which the material of this paper forms a part, required that a large number of records be run between March 25 and August 15. During this interval the position of the absorption at 4.225μ due to CO_2 was determined 76 times, a number large enough to permit a study of the non-temperature shifts. To show the nature of these shifts without tabulating the entire number of observations, there have been included in Table I selected groups of consecutive observations, the groups being spaced at equal intervals throughout the total number of observations. The third column of this table gives the locations of this line in terms of Veeder counter readings as taken directly from the records made on the dates and at the temperatures given in the first and second columns. These Veeder counter readings show a variation of 53 Veeder counter units between the extreme values. When the temperature correction of 5 Veeder counter units per degree departure from 22°C is applied the numbers of the fourth column are obtained. They represent what the observations on the position of this line would have been had the temperature of the prism been maintained at the standard temperature of 22°C. It is evident that these numbers decreased as the investigation progressed. The records from which the calibration data were obtained were made in April and the position of this CO_2 line at that time corresponded to a Veeder counter reading of 89,820, the temperature of the prism being 22°C. Taking 89,820 accordingly as the accepted position of this line at the standard temperature, the numbers in the fifth column measure the shifts in the positions of this line due to causes other than temperature variations. An inspection of the table shows the constancy of the positions of this line over the short time intervals embraced by the individual groups, while exhibiting the considerable changes which occur over longer intervals. This shift increases with time, but is not proportional to it; rather as has been said, it is dependent upon the amount the spectrograph is used. In conformity with this view the greatest shift occurred in July, the time of most intensive usage. During these months while spectra were being recorded, it was customary to apply the temperature corrections to the Veeder counter readings giving the location of the lines, and to this resulting value

add the number due to the mechanical shift. These latter numbers are in the sixth column and, if due to wear, should be constant for short-time intervals. As these numbers added to those of column four locate the position of the 4.255μ CO_2 line at 89820 within one or two Veeder counter units, so any correspondingly sharp line may be determined within these same limits.

CALIBRATION

In calibrating the spectrograph, the generally accepted method of using absorption lines whose wave-lengths have been determined by grating measurements is employed here. However, if the grating spectra are to be suitable for calibration purposes, the two spectra should have a one-to-one correspondence between the absorption lines. Should a grating spectrum be obtained at a resolution higher than that of the prism instrument, it may be that several absorption lines of that spectrum will combine to form one absorption line in the prism spectrum. It is not satisfactory, generally, to weigh the various components and use the weighted mean for determination of the wave-length of the single line. Hence, it was necessary to redetermine all of the grating spectra used in connection with this calibration, having first adjusted the resolution of the grating instrument in each case to be equal to that of the prism recorder for every spectrum measured. Under these circumstances, the spectra of a given region by the two spectrographs are practically identical and there is no ambiguity in the selection of corresponding lines. The requirements of this calibration call for a lower resolution than is employed in the most recently reported measurements of the ammonia and water-vapor spectra. Accordingly, the data on these two substances tabulated here should not be used in theoretical or other work requiring the highest possible resolution.

The calibration data are given here only for the region between 5μ and 15.4μ. This is the extent of the spectral region to which sodium chloride is best adapted, hence the region in which this material may be used for precise measurements. It is desirable to use for calibration, only substances which are easily handled and readily obtained. Therefore, water, ammonia, and carbon
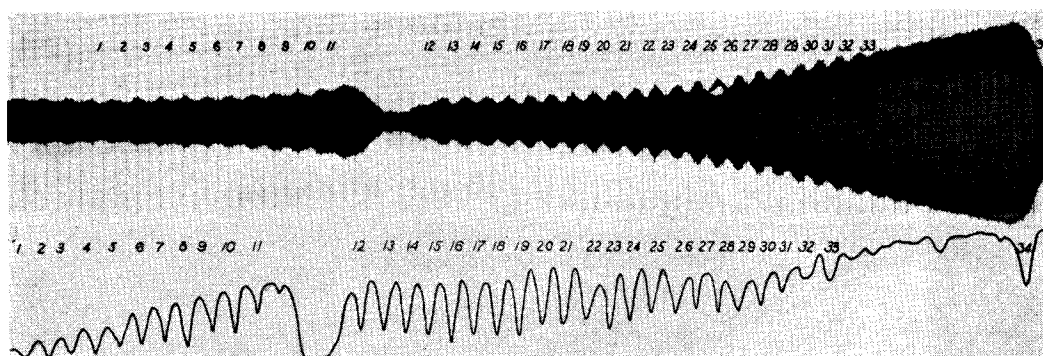
FIG. 2. Prism and grating spectra of carbon dioxide 15.4μ to 13.9μ.

dioxide, all in the vapor phase, were employed. The fine structure of the spectra of these three substances provides over 150 points in the above-mentioned region from which to determine the calibration curve which is obtained by plotting as abscissae the readings of the Veeder counters on the prism spectrograph, and as ordinates the wave-lengths measured on the grating spectrograph. Drawing a smooth curve through this large number of points minimizes the errors which are made in determination of individual points, and adequately corrects for any variation which may be due to irregularities in the driving mechanism. A smaller number of points, each determined several times for greater accuracy, would have sufficed as well for the calibration curve but would not have eliminated possible instrumental errors to the same extent as now obtains.

Thirty-four points are supplied between 15.4μ and 13.9μ by CO_2 with its rotational fine structure separation of 1.6 cm^{-1}. The fine structure in this region is shown in Fig. 2, the upper half being a reproduction of a prism recording while the lower half represents the plotted data obtained from the grating spectrograph, the corresponding absorption lines being numbered alike in the two spectra. The wave-length and frequency values for these absorption lines are given in Table II. The grating spectrum was previously described by Martin and Barker,[7] but is obtained again because the original data did not provide information thought to be essential to this calibration.

[7] P. E. Martin and E. F. Barker, Phys. Rev. **41**, 291 (1932).

The second substance used is ammonia which provides 71 points between 14μ and 8μ. The grating spectra have previously been published at both higher[8] and lower[9] resolution, but none of them could be used in this calibration since the one-to-one correspondence between absorption lines of the two spectra did not exist. The ammonia spectra with their absorption line correspondence indicated by the same numbers are shown in Fig. 3. The wave-length and frequency values are contained in Table III. Possibly it should be explained that the recording

TABLE II. CO_2 values used in making calibration curves.

Designation	Wave-length (μ)	Frequencies (cm^{-1})	Designation	Wave-length (μ)	Frequencies (cm^{-1})
1	15.408	649.0	19	14.652	682.5
2	15.371	650.6	20	14.617	684.1
3	15.336	652.1	21	14.583	685.7
4	15.300	653.6	22	14.549	687.3
5	15.263	655.2	23	14.512	689.1
6	15.228	656.7	24	14.482	690.5
7	15.192	658.2	25	14.449	692.1
8	15.158	659.7	26	14.414	693.8
9	15.120	661.4	27	14.380	695.4
10	15.086	662.9	28	14.346	697.1
11	15.051	664.4	29	14.315	698.6
12	14.894	671.4	30	14.281	700.2
13	14.859	673.0	31	14.249	701.8
14	14.825	674.5	32	14.213	703.6
15	14.791	676.1	33	14.175	705.5
16	14.755	677.7	34	13.875	720.7
17	14.721	679.3			
18	14.686	680.9			

[8] H. Y. Sheng, E. F. Barker, and D. M. Dennison, Phys. Rev. **60**, 786 (1941).
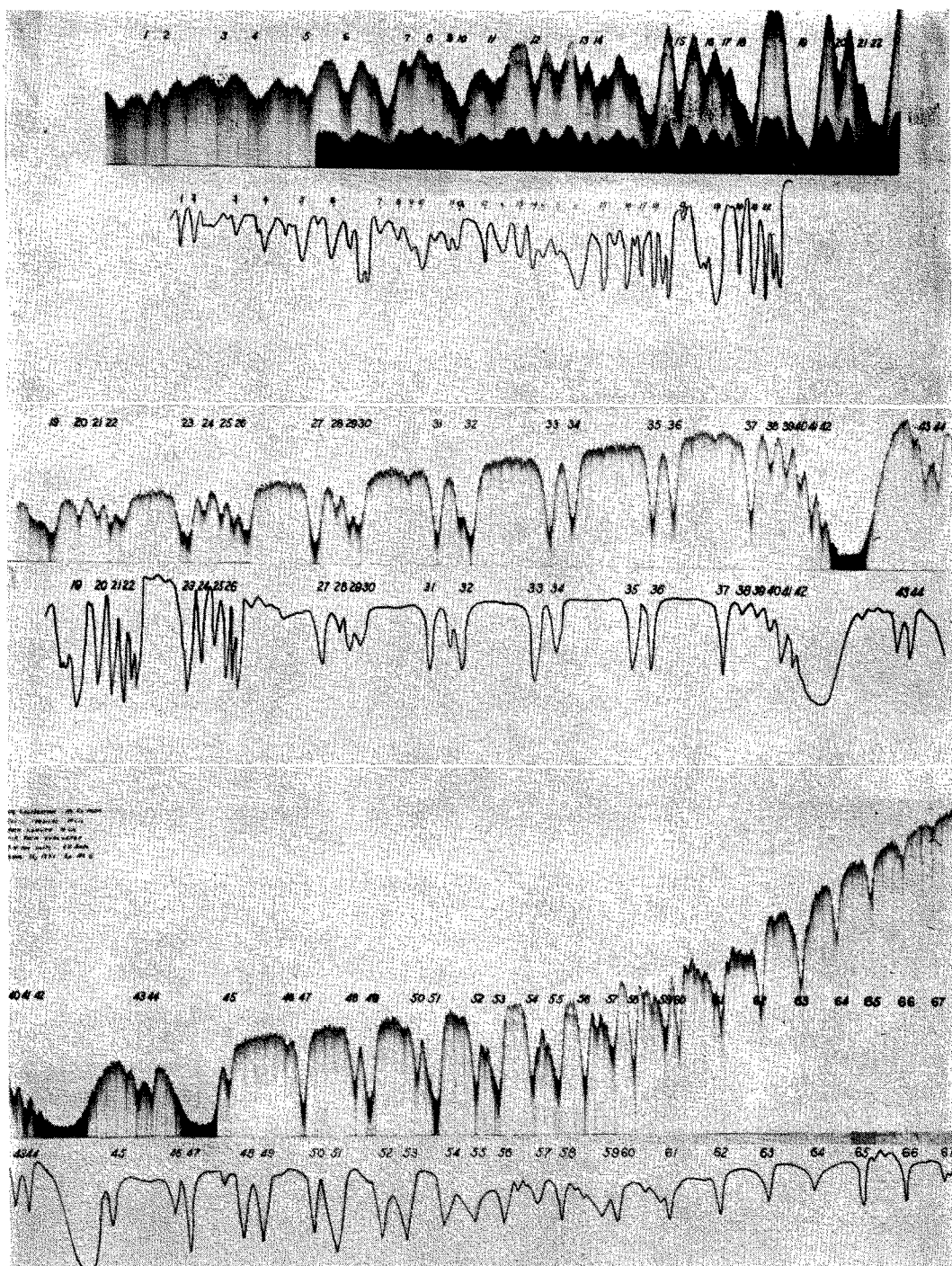[9] E. F. Barker, Phys. Rev. **33**, 684 (1929).

FIG. 3. Prism and grating spectra of ammonia 14μ to 8μ.

light point, with the Firestone amplifier, swings equally to each side of the equilibrium position. This results in the lower half of the record being

a mirror image of the upper half. Such a double-prism record with its fiducial lines forms the upper part of Fig. 2. To conserve space, the

TABLE III. NH₃ values used in making calibration curves.

Desig-nation	Wave-length (μ)	Fre-quencies (cm⁻¹)	Desig-nation	Wave-length (μ)	Fre-quencies (cm⁻¹)
1	14.035	712.5	34	11.459	872.7
2	14.000	714.3	35	11.257	888.3
3	13.891	719.9	36	11.206	892.4
4	13.821	723.5	37	11.008	908.4
5	13.722	728.8	38	10.956	912.7
6	13.651	732.5	39	10.917	916.0
7	13.528	739.2	40	10.883	918.9
8	13.482	741.7	41	10.852	921.5
9	13.448	743.6	42	10.819	924.3
10	13.417	745.3	43	10.540	948.8
11	13.357	748.7	44	10.504	952.0
11a	13.334	750.0	45	10.284	972.4
12	13.268	753.7			
12a	13.219	756.5	46	10.114	988.7
			47	10.073	992.8
13	13.176	759.0	48	9.929	1007.2
14	13.142	760.9			
14a	13.116	762.4	49	9.876	1012.6
14b	13.084	764.3	50	9.734	1027.3
14c	13.031	767.4	51	9.673	1033.8
15	12.968	771.1			
			52	9.552	1046.9
16	12.915	774.3	53	9.484	1054.4
17	12.876	776.6	54	9.378	1066.3
18	12.845	778.5			
18a	12.713	786.6	55	9.295	1075.8
			56	9.216	1085.1
19	12.684	788.4	57	9.123	1096.1
20	12.627	792.0			
21	12.589	794.3	58	9.057	1104.1
			59	8.949	1117.4
22	12.558	796.3	60	8.905	1123.0
23	12.381	807.7			
24	12.343	810.2	61	8.762	1141.3
			62	8.623	1159.7
25	12.309	812.4	63	8.490	1177.9
26	12.277	814.5			
27	12.075	828.2	64	8.362	1195.9
			65	8.241	1213.4
28	12.035	830.9	66	8.123	1231.1
29	12.005	833.0			
30	11.978	834.9	68	7.902	1265.5
31	11.793	848.0			
32	11.709	854.0			
33	11.518	868.2			

prism records for ammonia and water vapor have been cut along their center line and only the upper half shown above the drawings of the corresponding grating spectra.

The 6-μ water band has been investigated several times,[10] but again no previous spectrum contained the desired information due to differences in resolution, though the strongest lines of

the early grating spectra agree quite closely with the values given here. Figure 4 and Table IV present the calibration data for the 51 absorption lines used from water vapor data.

Table V gives the path lengths and pressures of the vapors used in making this calibration.

ACCURACY ATTAINABLE

The absorption lines which are used in the calibration are all sharp lines, and obtained when the spectrograph was run most favorably. Hence, errors of only 1 or 2 seconds of arc are likely in

TABLE IV. H₂O values used for plotting calibration curve.

Desig-nation	Wave-length (μ)	Fre-quencies (cm⁻¹)	Desig-nation	Wave-length (μ)	Fre-quencies (cm⁻¹)
1	7.930	1261	28	6.267	1596
2	7.860	1272	29	6.180	1618
3	7.608	1314	30	6.156	1624
4	7.577	1320	31	6.107	1637
5	7.460	1340	32	6.066	1649
6	7.335	1363	33	6.009	1664
7	7.269	1376	34	5.983	1671
8	7.204	1388	35	5.933	1685
9	7.162	1396	36	5.884	1700
10	7.113	1406	37	5.820	1718
11	7.043	1420	38	5.762	1736
12	6.989	1431	39	5.712	1751
13	6.957	1437	40	5.637	1774
14	6.903	1449	41	5.574	1794
15	6.855	1459	42	5.520	1812
16	6.820	1466	43	5.463	1830
17	6.784	1474	44	5.416	1846
18	6.709	1491	45	5.348	1870
19	6.675	1498	46	5.288	1891
20	6.631	1508	47	5.233	1911
21	6.586	1518	48	5.204	1922
22	6.566	1523	49	5.144	1944
23	6.515	1535	50	5.081	1968
24	6.486	1542	51	5.017	1993
25	6.411	1560			
26	6.367	1571			
27	6.339	1578			

TABLE V. Conditions for obtaining prism calibration spectra.

Substance	Wave-length region	Path length	Pressure
CO₂	15.4–13.9μ	100 cm	15 mm
NH₃	14 –12.5μ	10 cm	250 mm
NH₃	12.7– 8μ	10 cm	100 mm
NH₃	8.5– 7.8μ	10 cm	750 mm
H₂O	8 – 5μ	500 cm	air

[10] W. W. Sleator, Astrophys. J. **48**, 125 (1918); W. W. Sleator and E. R. Phelps, Astrophys. J. **62**, 28 (1925); H. H. Nielsen, Phys. Rev. **59**, 565 (1941).
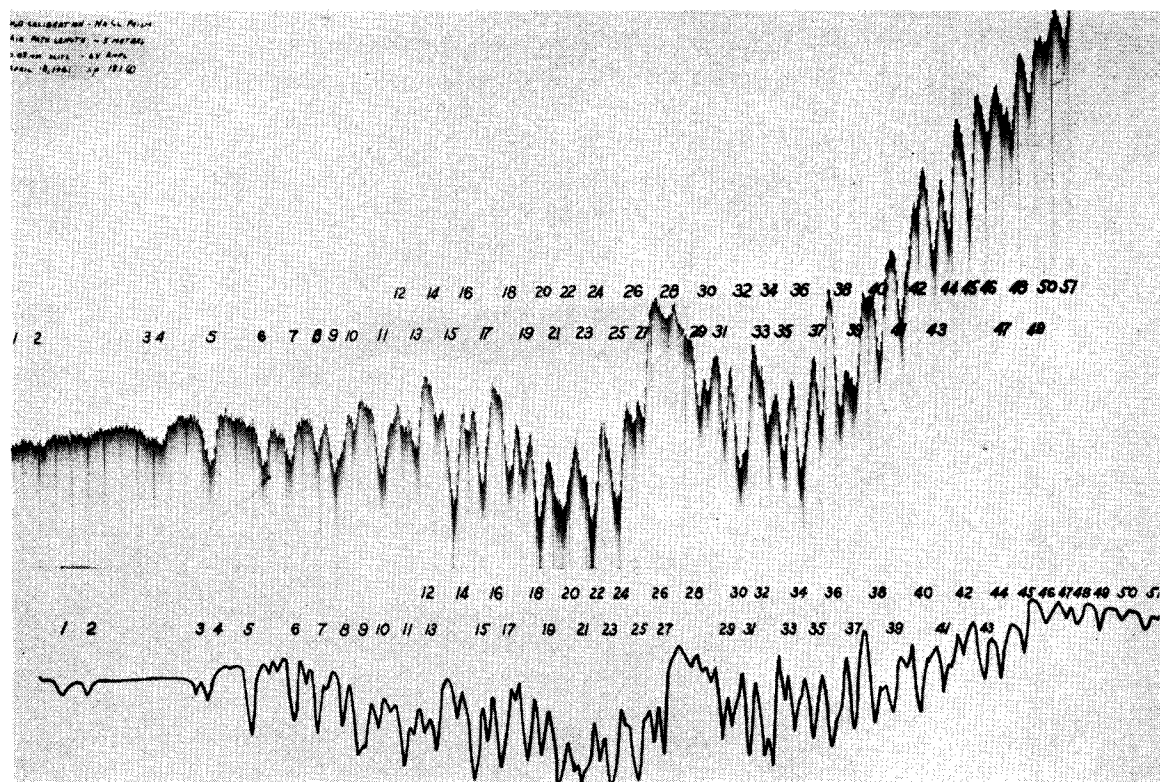
FIG. 4. Prism and grating spectra of water vapor 8μ to 5μ.

the location of the centers of any equally sharp absorption lines in the prism spectra.

Without attempting to estimate the accuracy of the various measurements connected with the determination of the wave-length of a line by grating methods it will be sufficient to say that experience shows that such measurements are accurate to within one unit in the third decimal place. We consider our grating values to be correct within these same limits. Assuming then that the Veeder counter readings of the prism lines are correct to 2 Veeder counter units and the wave-lengths of these same lines accurate to 0.001μ, we have chosen to combine these data for calibration by drawing a large-scale calibration curve. The scale employed assigns 5 Veeder counter units per mm as abscissae and 0.002μ per mm as ordinates. On this scale it appears to be possible to draw a calibration curve which permits preserving the accuracy so far achieved. To demonstrate to what degree this is true there have been collected in Table VI the results of

direct grating and prism measurements on the fine structure lines of the ethane band at 12μ which have a frequency separation of 2.5 cm^{-1}. The wave-length values given in the first column are those due to Owens and Barker[11] while the values in the second and third columns were obtained more recently by L. R. Posey. The fifth column contains the values of these same lines as recorded with the prism instrument, the methods of evaluation being those presented in this paper. It appears that these prism values for this spectral region are obtained with substantially the same accuracy as the grating values, the order of inaccuracies being about $\pm0.001\mu$. Similar considerations in the neighborhood of 5μ show that an accuracy of $\pm0.005\mu$ may be expected there. It should be noted that the wave-lengths here recorded by the vacuum prism recorder are the proper values of these wave-lengths at atmospheric pressure, since the

[11] R. G. Owens and E. F. Barker, J. Chem. Phys. 10, 146 (1942).

wave-lengths used in the calibration curve are the grating values obtained at atmospheric pressure.

In recognition of temperature and instrumental changes, it has been the practice here in former years when accurate measurements were to be made, to determine the position of the 4.225-μ or 15-μ CO_2 absorption before and after the sample under investigation was recorded. In this manner both the temperature and instrumental shifts may be corrected to a fair approximation. This practice is probably a common one with others where accuracy is sought.

CONCLUSIONS

The investigation of which this report is a part leads to the following conclusions:

1. It is necessary to operate the spectrograph at a speed consistent with the response time of the thermopile and the characteristics of the amplifier and recorder.

2. Changes in the temperature of the prism as small as 0.5°C have an effect on wave-length measurements. This may be remedied by temperature control or by an empirical correction.

3. It is necessary to make frequent tests to determine what shifts of the spectrum may be caused by mechanical imperfections of the operating mechanism of the spectrograph. Suitable corrections must be made for any shift detected.

TABLE VI. The fine structure of ethane band. Grating and prism data compared.

Grat. 1940	Grat. 1941	Grat. 1942	Mean	Prism 1942	Diff.
11.891	11.893	11.892	11.892	11.892	0
11.929	11.929	11.930	11.929	11.929	0
11.967	11.968	11.967	11.968	11.969	+1
12.006	12.006	12.006	12.006	12.007	+1
12.044	12.043	12.044	12.044	12.047	+3
12.083	12.084	12.085	12.084	12.084	0
12.121	12.123	12.123	12.122	12.123	+1
12.159	12.159	12.160	12.159	12.157	-2
12.199	12.200	12.200	12.200	12.200	0
12.240	12.239	12.240	12.240	12.241	+1
12.278	12.279	12.279	12.279	12.280	+1
12.318	12.319	12.319	12.319	12.318	-1
12.358	12.358	12.358	12.358	12.357	-1
12.397	12.397	12.398	12.397	12.396	-1

4. Since an empirical calibration requires one-to-one correspondence between the absorption lines of the prism and grating spectra, data are presented for use in calibrating a sodium chloride prism in the spectral region between 5μ and 15.4μ.

5. In this particular spectrograph, by making the above corrections and plotting a suitable calibration curve, an accuracy of $\pm 0.001\mu$ or 0.05 cm^{-1} at 15μ and $\pm 0.005\mu$ or 2 cm^{-1} at 5μ may be obtained.