The Spectroscopy of the Far Infra-Red[1]

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BY spectroscopy of the far infra-red I have in mind not the early pioneering in that field, but rather those subsequent developments by which the methods and purposes of the near infra-red spectroscopy are being extended to the far infra-red, and in particular I am interested in the molecular band spectra to be found in this little known region. How undeveloped this must be, will appear when it is noted that the papers presenting the results of investigations in band spectra of the far infra-red have not averaged one a year since they first began to appear fifteen years ago. My present purpose is, therefore, not to present a critical review of progress in a highly developed field of research, but rather to present a plea for the far infra-red region as a field of investigation, and to show that this region may provide information of great value not found elsewhere or, at least, not easily obtainable from the more accessible regions of the spectrum. Experimental methods will be described showing results which I hope will form convincing evidence that this field of spectroscopy, long dormant, can now, for the first time, be made to contribute its proper share to the development of molecular theory.

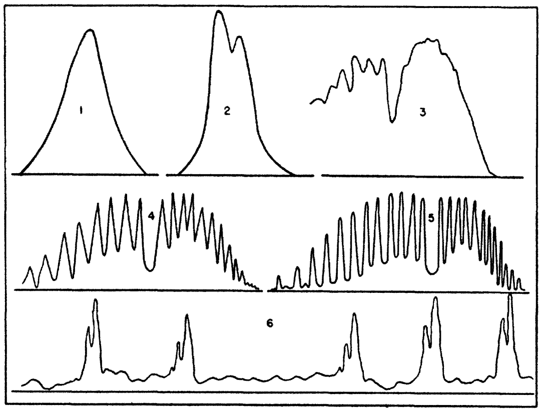

FIG. 1. The band of HCl at 3.5μ. 1, Angstrom and Palmer, 1893, width of slits 4000A. 2, Burmeister, 1914, slits 400A. 3, von Bahr, 1914, slits 100A. 4, Brinsmade and Kemble, 1917, slits 70A. 5, Randall and Imes, 1919, slits 39A. 6, Meyer and Levin, 1929, slits 7.5A.

The first reaction when considering research in the far infra-red will undoubtedly be that great experimental difficulties are inherent in such work. It must be acknowledged too that many people think the desired information may be obtained more easily from the vibration-rotation bands in the near infra-red or from Raman spectra, thus making research in the far infra-red itself rather without point. This, however, is not the case since there are many problems that cannot be adequately attacked in this indirect manner. For their solution by measurements in the far infra-red a very high grade grating spectrograph of exceptionally high resolving power is required. Indeed, the accuracy of measurement necessary and the resolution demanded are of the same order as are now required for the most exacting work with vibration-rotation spectra in the near infra-red. Just how much the interpretation of band spectra depends upon high resolution is strikingly shown by the collection of curves, Fig. 1, representing the historical development of the vibration-rotation bands of HCl. The observations that Angstrom made in 1893, show the band at 3.5μ to be a single broad absorption region, while the measurements of Meyer and Levin in 1929, show it to have not merely a fine structure but to have each line of this structure a doublet due to the isotopes of chlorine. Here we have a telling picture of the increased information to be obtained with increased resolution. Angstrom had to use slits 4000A wide to get enough energy to record this absorption line. Each subsequent improvement in the equipment which permitted narrower slits and greater resolution resulted in the fine structure of this band becoming more definite and measurable. Only in the final inves-

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[1] Address as retiring President of the American Physical Society, given at Indianapolis, December 28, 1937.

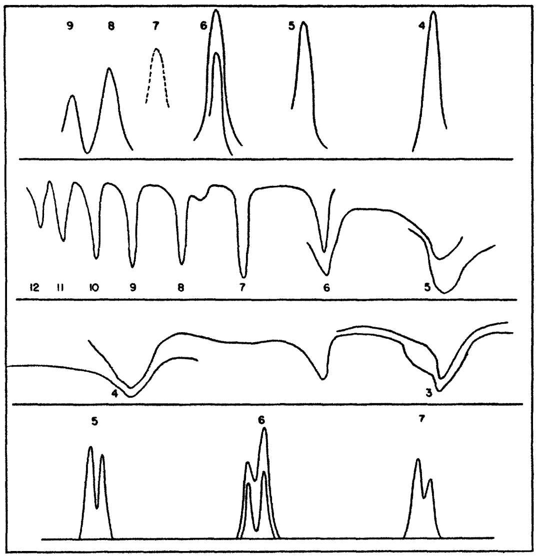

FIG. 2. Rotational bands of ammonia. Upper section, Badger and Cartwright 1929. Middle sections, Barnes 1935. Lower section, Wright and Randall 1933.

tigation, in which the slits were but 7.5A wide, is the fine structure fully developed.

The most powerful spectrographs now used in the near infra-red give a resolution at 3μ which permits sharp lines to be separated which are but 1 cm^{-1} apart. At 10μ and beyond this, possibility of separation is increased to 4 or 5 tenths of a frequency unit. This resolution combined with an accuracy of measurement of wave-length corresponding to 0.005μ or of frequency to 0.05ν is quite sufficient to meet the requirements of the theoretical physicist for many problems in the field of molecular structure. If the data of the far infra-red region are to be used in combination with those from the near infra-red for the development of theory, then the same accuracy of measurement and the same high resolution must be attained there also.

After the development in 1920 of the present, all but universally used, prism-grating spectrograph for work with band spectra in the near infra-red, I became interested in the design of a spectrometer which would be equally effective for the far infra-red. This instrument, which I shall now describe, together with its accessory apparatus has been in process of development over a period of about 20 years. While gradual progress has been made during this time, the goal set, for accuracy of measurement and completeness of resolution, proved, until quite recently, to be too high for attainment.

Experimentally the great difficulty of the far infra-red is the minute amount of energy available. For work in this region the physicist wishing large dispersion and high resolution has a problem comparable to that of the astronomer who requires fine definition, and his solution must be along the lines adopted by the astronomer; namely, to capture and to conserve the greatest possible amount of radiant energy. This means, in the first place, a spectrograph of large aperture and relatively wide slits. If the radiation thus introduced into the instrument is conserved to the utmost through the use of collimating mirrors of short focal length and coarse wire or laminated gratings which suppress spectra of even orders, the resulting spectrum will contain the maximum amount of energy. Under these circumstances the chances are most favorable for the measurement of the distribution of energy in the spectrum. Such an instrument has of necessity very small resolution. Nevertheless, if one chooses gases whose rotational spectra are simple and have an open structure, it may be possible to make measurements that are of great value to molecular theory. This, indeed, is what Czerny[2] did in 1925 with the rotation spectra of the halogen hydrides and what Badger and Cartwright[3] did in 1929 for ammonia, as shown in the upper section of Fig. 2. Possibilities of this kind are comparatively limited,

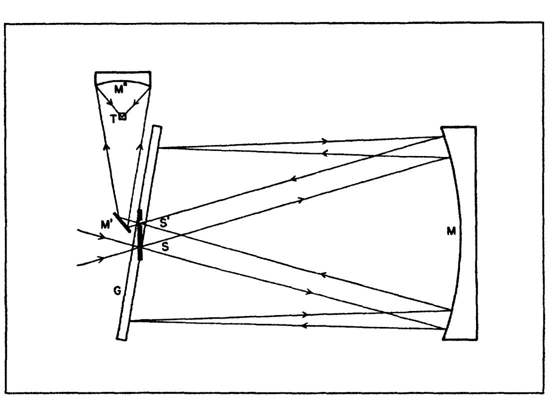

FIG. 3. A horizontal cross section of the spectrometer in the plane containing the mirror center.

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[2] Czerny, Zeits. f. Physik 34, 227 (1925).

[3] Badger and Cartwright, Phys. Rev. 33, 692 (1933).

FIG. 4. The Michigan ruling engine.

however, and spectrographs of such low resolving power find no proper place in the analysis of complex spectra, as has been abundantly demonstrated when they have been used to measure the rotation spectrum of water vapor.

The best spectrograph of this type, both in its resolving power and in its flexibility, is undoubtedly that described in 1934 by Barnes.[4] With it, the rotational spectrum of ND_3 was measured and that of NH_3 extended to ten lines as shown in Fig. 2. The doubling of the NH_3 lines was indicated only by a broadening in the lines of longest wave-length however. The slits of this spectrograph covered at 50μ a frequency range of 4.42ν, at 100μ a range of 1.67ν and at 150μ one of 1.14ν, too large to measure the fine structure of the rotational lines of NH_3. This is in accordance with experience which has shown that the slit widths should be but a small fraction of the line separation to be measured.

Applied to water vapor this spectrograph gave many times the number of lines previously resolved by any of the other short focus spectrographs which used wire or laminated gratings; but its resolution was still not sufficient to permit a satisfactory interpretation of this spectrum, with a consequent determination of the rotational levels of the molecule.

One factor in obtaining large dispersion is a collimating mirror of long focal length. Long focal length is, however, incompatible with a large aperture unless the mirror be correspondingly large. Our laboratory is fortunate in having two such mirrors, which are the two halves of a large parabolic mirror given to me after it had been accidentally broken apart. The diameter is 2 feet and the focal length 3 feet. A collimated beam from one of these parts will fill a grating having a ruled surface of 10×22 inches, when the illumination is oblique as it is in ordinary use. With the entrance and emergent slits immediately above the grating, close to the optical axis of the mirror, we have a spectrograph possessing exceptional qualities. It collects a great deal of energy, the axes of the incident beam and emergent beam nearly coincide with the mirror axis giving minimum extra axial aberration, the long focal length used in conjunction with echelette gratings ruled with several hundred lines per inch give great dispersion, while the excellence of the optical parts, the smallness of the grating constants, the freedom from image distortion and the use of comparatively narrow slits all count toward very

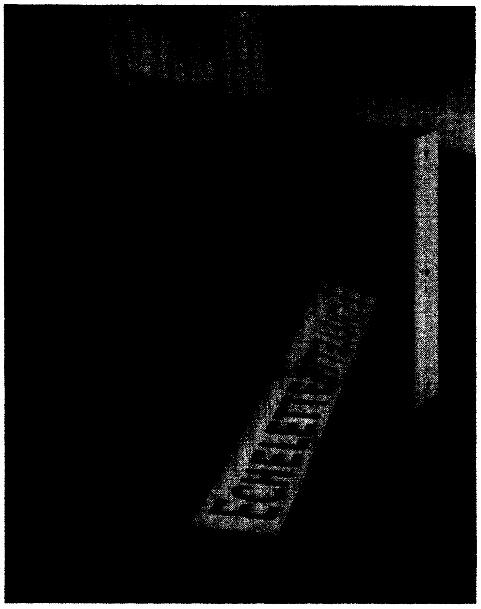

FIG. 5. The grooves of an echelette grating have plane sides, one wide, inclined at about 25° to the face of the grating, and one narrow, nearly perpendicular to the face. In Fig. 5, the paper strip is normal to the planes of the wide or working sides of the grooves.

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[4] Barnes, Phys. Rev. **47**, 658 (1935) and Rev. Sci. Inst. **5**, 237 (1934).

high resolution. This spectrometer was conceived and built years too soon, since there was at that time no detecting system sufficiently sensitive to measure the distribution of energy in so extended a spectrum. When it was discovered that enclosing a thermopile in a high vacuum increased its sensitivity many times, and when amplifying devices were available which further increased the sensitivity of the detecting systems hundreds of times, this spectrograph (Fig. 3) became immediately a very powerful instrument, possessing great dispersion and a very high resolution. It was first described in 1932.

All other spectrographs for use in the far infra-red have used wire or laminated gratings which do certainly possess definite advantages. However, it seemed from the first that the echelette grating, originally introduced by Wood, was the one which could ultimately give the best results, since it could be ruled to concentrate a large part of the available energy in a narrow spectral range. Accordingly, years were spent in developing this grating for our purpose. Starting with trial gratings ruled on the shaper of the instrument shop, there followed several years' work with one of the Rowland engines borrowed from Johns Hopkins. This in turn was succeeded by our own engine (Fig. 4) designed especially to rule echelette gratings of large size. These gratings now are of excellent quality, thanks largely to the designer of the engine, Captain De Khotinsky, and to his successor Mr. Paul Weyrich. For work beyond 20μ, gratings with ruled surfaces 10×20 inches in area have been developed under the general direction of Professor Barker. For the region between 18 and 25μ satisfactory results have been obtained with gratings which are ruled with 1200 lines per inch, from 25 to 40μ with 900 lines, between 40 and 70μ with 360 lines, and for work from 70 to 140μ with 120 lines per inch.

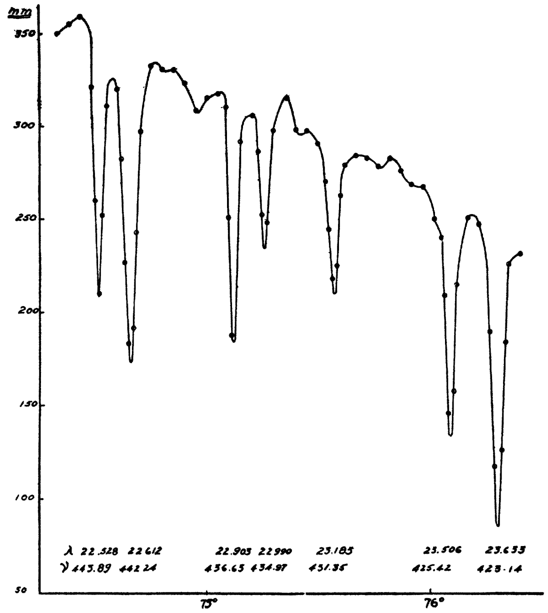

FIG. 7. This curve represents the first set of observational data on water vapor beyond 18μ. Single galvanometer readings were taken for each minute of arc through which the 1200 line/in. grating was turned. The plot indicates the steadiness and sensitivity of the equipment, as well as the resolution obtainable.

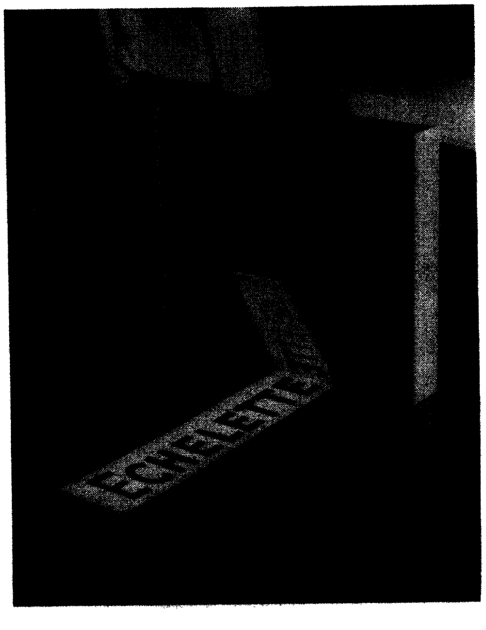

FIG. 6. The paper strip is normal to the surface of the grating.

The narrow region in which the grating concentrates its energy is conveniently called the "blaze." As is well known, the echelette grating achieves this result through giving the grooves, composing the ruled surface, flat sides, properly inclined to the surface of the grating. Such a grating is shown in Figs. 5 and 6. Experience has shown that an angle of about 24° between the grating face and the working side of the groove is

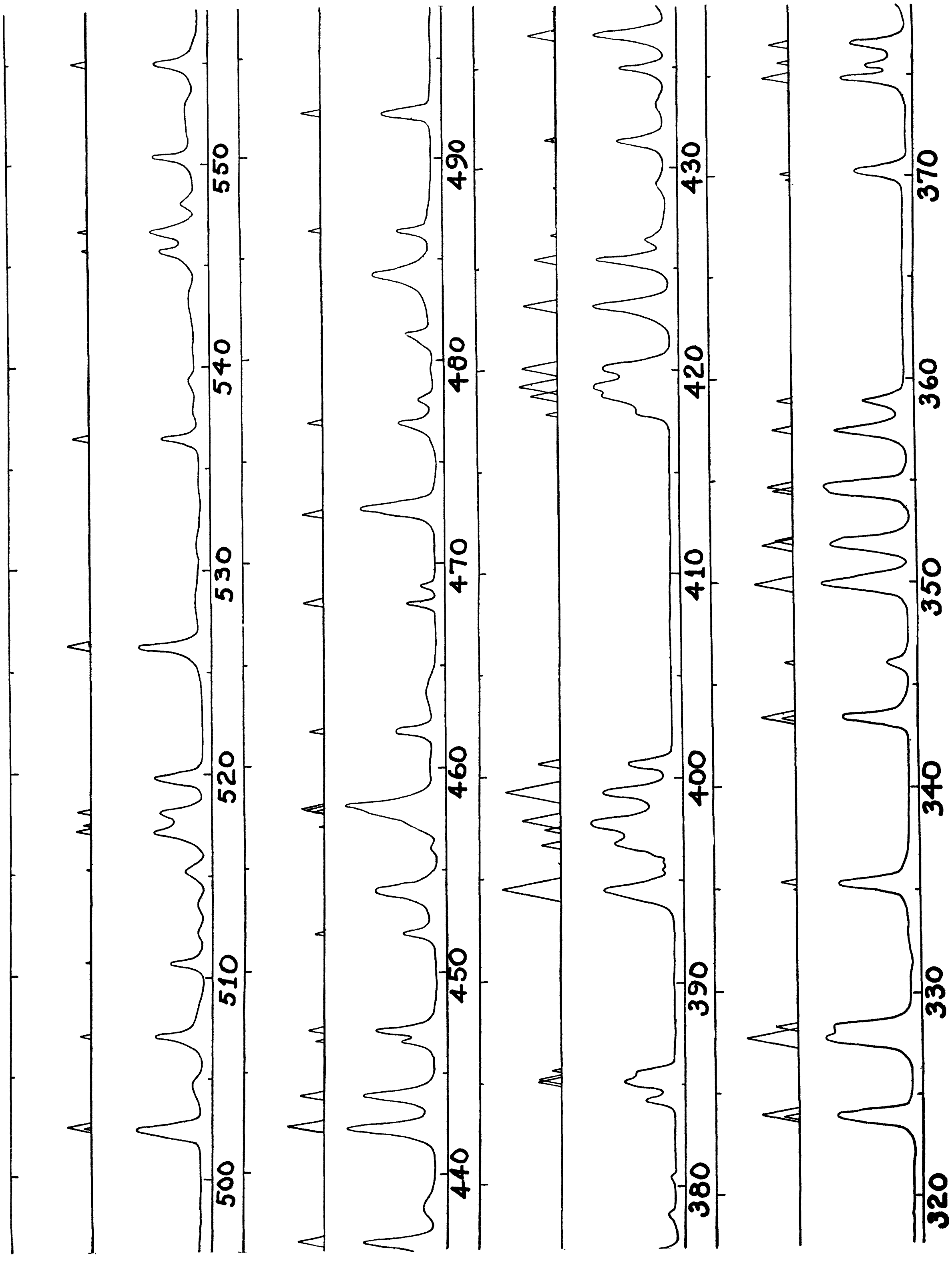

FIG. 8. Analysis of the rotational spectrum of water vapor.

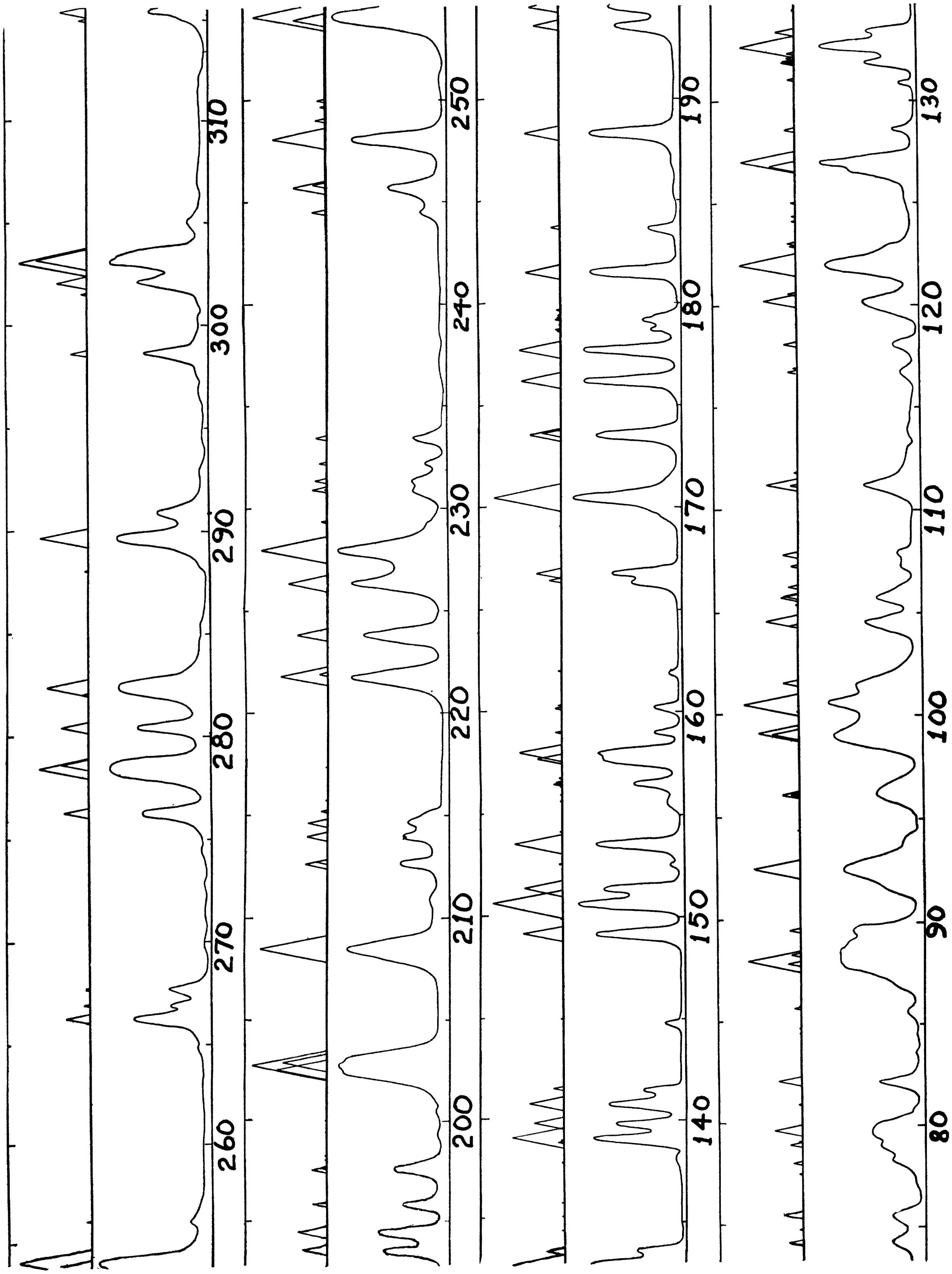

FIG. 9. Analysis of the rotational spectrum of water vapor.

well adapted to most purposes. The gratings listed above are all ruled with this approximate angle and locate the blaze at 18μ for the grating with 1200 lines per inch, at 23μ with the 900 line grating, at 57μ with the 360 line grating and at 90μ with the one having 133 lines per inch. It is more satisfactory to work at some distance from either side of the blaze than in the blaze itself. This is because the very great concentration of short wave-length energy here in the form of higher orders makes it difficult to get the requisite purity of spectrum. The results to be reported later depend to a great degree for their excellence upon the superior quality of these gratings, which conserves the energy quite successfully in a single spectrum, and gives a very sharp definition to the lines. Both of these characteristics aid in producing the large deflections observed, which generally vary from 50 to several hundred mm.

Among the other lines of development carried on, has been that of growing large crystals from materials increasingly transparent to this long wave-length radiation. Two of the physicists interested in this phase of the work have obtained very satisfactory results; Dr. John Strong in 1930, and Dr. Katherine Chamberlain, at the present time. As a result we have prisms of good size of KCl, KBr and KI which permit us to extend the near infra-red spectrum somewhat into the far region by prism methods. The main purpose, however, of this continuing program of crystal growing is to produce materials for shutters which are transparent farther and farther out in the long wave-length region.

After obtaining the maximum purity possible through reflection and through absorption, there always remain appreciable quantities of shorter wave-length radiation. This undesired residuum can, however, be rendered quite ineffective by constructing the shutters of material which are transparent to it. For work beyond 40μ, KBr plates are used which are sufficiently thin to transmit radiation up to 30μ; KI plates when quite thin will transmit well to 45μ. This work is to be extended to the heavier alkali halides, with the expectation of obtaining a still further extension of transparency. These development programs are not limited to gratings and crystals, but are paralleled by similar ones on thermopiles, amplifiers, sources of radiation, and other phases of infra-red technique.

The first investigation with this spectrograph was reported in 1933,[5] when the rotation spectrum of water vapor from 60μ to 140μ was measured, lines as close as a single frequency unit being clearly resolved. Also several lines each of the rotation spectra of ammonia and phosphine were measured, those of ammonia showing (see Fig. 2), well resolved, the doublets predicted by Dennison, with a separation of 1.33 frequency units. While the data obtained at this time on water vapor, some 30 lines altogether, were not sufficiently extensive to permit a successful interpretation of its rotational spectrum, the measurements on the rotational lines of NH_3 did contribute materially to molecular theory, in that they substantiated the conclusions of Dennison[6] and his associates in their theoretical treatment of the NH_3 molecule. The data on NH_3 and PH_3 also made possible new computations of the moments of inertia of these molecules. The fact that the rotational lines of PH_3 showed no sign of doubling indicates that the P atom lies farther from the plane of the three H atoms than the N atom does in NH_3. This assumption is supported by the fact that the moment of inertia for PH_3, $A=6.221\times10^{-40}$ g cm^2 is larger than that of NH_3 which is, $A=2.782\times10^{-40}$ g cm^2.

The first investigation demonstrated quite amply that this spectrograph permitted that accuracy of measurement and degree of resolution for which the instrument was originally designed.

The next investigation to be completed was a continuation of the measurement of the rotation spectrum of water vapor, the region this time being from 18 to 80μ. The results were reported in 1937.[7] Because the apparatus had been made more steady, greater amplification could be used, and in consequence narrower slits. This increased the resolution so that lines 0.5 cm^{-1} could be clearly separated and measured. Results on water vapor are shown in Fig. 7. The accuracy with which sharp lines could be determined

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[5] Wright and Randall, Phys. Rev. **44**, 391 (1933).

[6] Dennison and Hardy, Phys. Rev. **39**, 938 (1932); Dennison and Uhlenbeck, Phys. Rev. **41**, 313 (1932).

[7] Randall, Dennison, Ginsburg, Weber, Phys. Rev. **52**, 160 (1937).

varied from 0.003μ around 20μ to somewhat more at 75μ. Throughout this entire range the accuracy in terms of frequency units was about 0.05. The spectral range covered by 1 mm slits is 0.009μ at 25μ, when the 1200 lines/in. grating is used, and becomes 0.032μ at 80μ with the 360 lines/in. grating. These figures again show that this spectrograph has attained the goal set; namely that it should equal in precision of measurement and in degree of resolution the best of the spectrographs used in the near infra-red.

For our present purpose the measured absorption lines, plotted (Figs. 8 and 9) on a frequency scale, may be compared to those predicted theoretically which are found on a plot running immediately above the measured results. Such a comparison shows no predicted line without a measured counterpart of corresponding frequency and intensity, while only a few of the 173 measured lines have no corresponding theoretical counterpart. This is due undoubtedly to the fact that the analysis did not include sufficiently high energy states. The completeness with which the rotational spectrum of water vapor has been analyzed may be judged partially by the fact that, of the 173 lines found, 160 are satisfactorily accounted for, and that 115 distinct rotational levels have been calculated, with an error generally less than 0.1 frequency unit. Such results also show very strikingly how competent the quantum theory is in interpreting such a complex and apparently chaotic arrangement of lines as these measurements show the rotational spectrum of water vapor to be.

The spectrograph just described is encased in a metal chamber, covered with Celotex, and has been a very satisfactory instrument for use with water vapor, since the amount of the latter could be easily varied, as experimental conditions required, with P_2O_5 as a dryer. With other materials, however, the situation is quite different, since their spectra are certain to be overlaid by that of water vapor as no amount of drying has served to remove the water sufficiently to prevent its spectrum from showing. For other gases, therefore, an apparatus which can be evacuated is very essential. The experience gained in building and using a vacuum prism-spectrograph,[8] which is self-recording, has aided greatly in the work of changing our large grating spectrograph to a similar instrument. This project has been completed with the collaboration of Professor Firestone. The tech-

FIG. 10. Spectrograph viewed from the rear, ready to be rolled into the vacuum case.

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[8] Randall and Strong, R.S.I. 2, 585 (1931).

FIG. 11. Spectrograph viewed from the front.

nical details of the methods used to accomplish these purposes would be out of place in this presentation, particularly as they are to be published soon. However, the chief features of the new vacuum instrument may be listed.

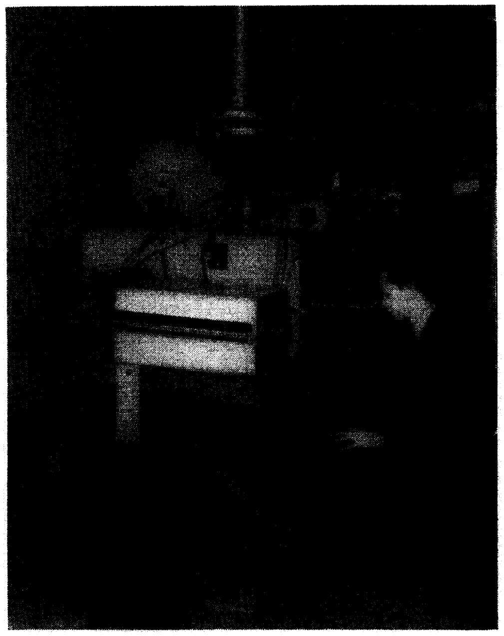

FIG. 12. View of spectrograph case showing outside attachments.

The grating spectrograph, a duplicate of the one used in the investigation of water vapor, has been mounted upon a heavy steel *I* beam. After the adjustment of the instrument has been made, this is rolled into the vacuum chamber (Fig. 10) and lowered to a predetermined position. Here it rests upon three points, completely uninfluenced by any movement of the walls of the chamber due to pressure changes. All the usual adjustments to be made on spectrographs, such as changes in widths and curvatures of the slits, refocusing upon thermoelement, reading of circle, hand rotation of grating, can be made from the outside without effect upon the vacuum, through ground vacuum-tight joints. A single outside mechanism, motor driven, rotates the grating (Fig. 11), turns a Veeder counter for measuring the angle of rotation of the grating, and flashes a light for registering a reference line across the spectrum, as it is being recorded. This flash occurs every 30″ of arc through which the grating turns. A second synchronous motor is geared to operate the shutter within the spectrograph before the entrance slit. The period with which the shutter vibrates is timed to agree with the period of the impulse which the Firestone[9] amplifier passes. Disturbances causing drifts, and occasional fluctuations lacking this period, are not passed and amplified. As a result, the observed drifts and accidental displacements are very small. The complete instrument is shown in Fig. 12.

This transformed spectrograph has been subjected to an extensive test, by recording the spectrum of water vapor between 40 and 75μ (Fig. 13). The records were made without preliminary practice by an assistant who was very skillful in operating the prism recording spectrograph, but who had had no experience with this new recorder. The records show that

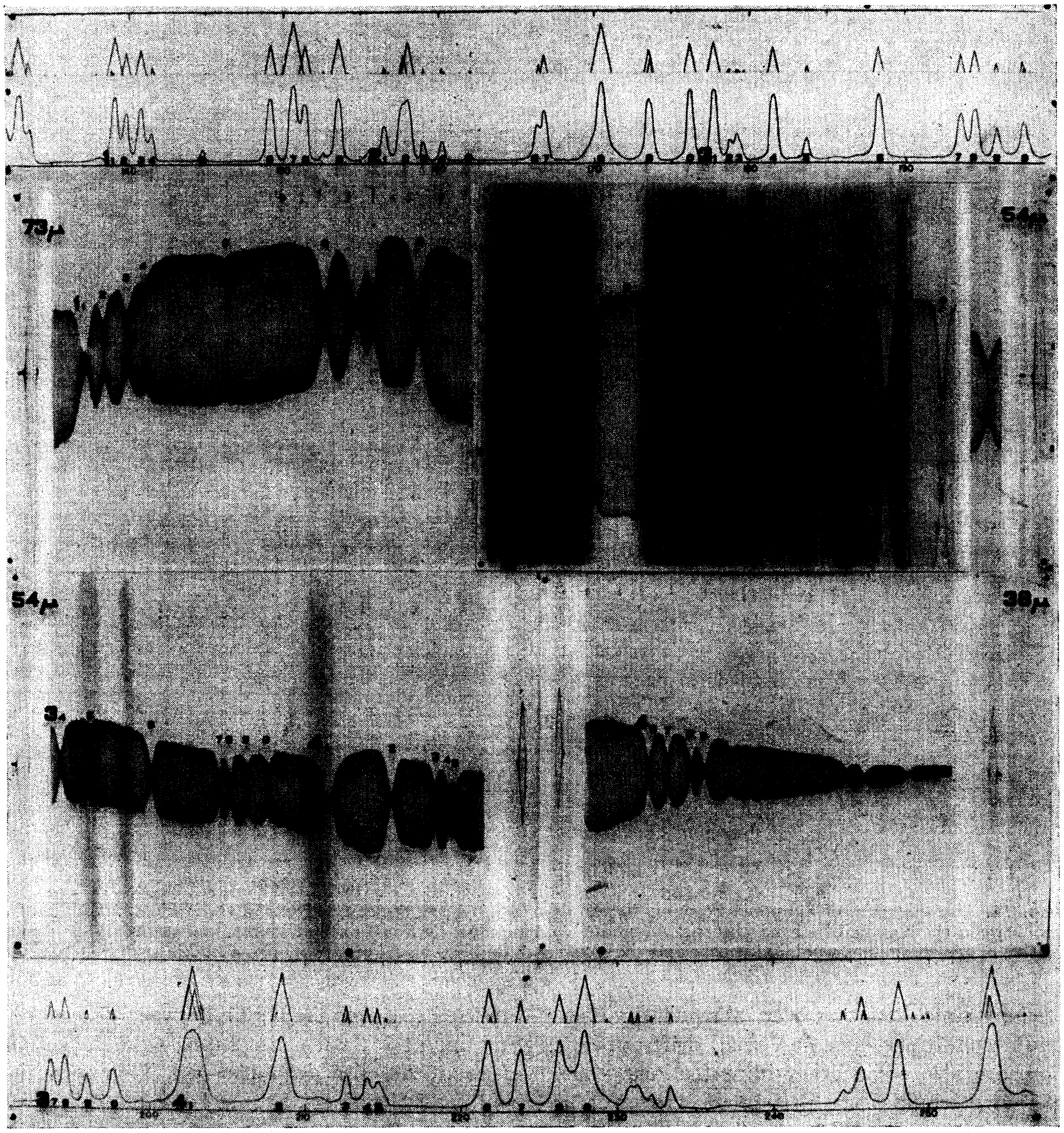

FIG. 13. Four photographically recorded records of the rotational spectrum of water vapor between 75 and 40μ. Above and below are plotted the mean wave-lengths of the lines obtained with the manual spectrograph. The corresponding lines bear the same numbers.

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[9] Firestone, R.S.I. 3, 163 (1932).

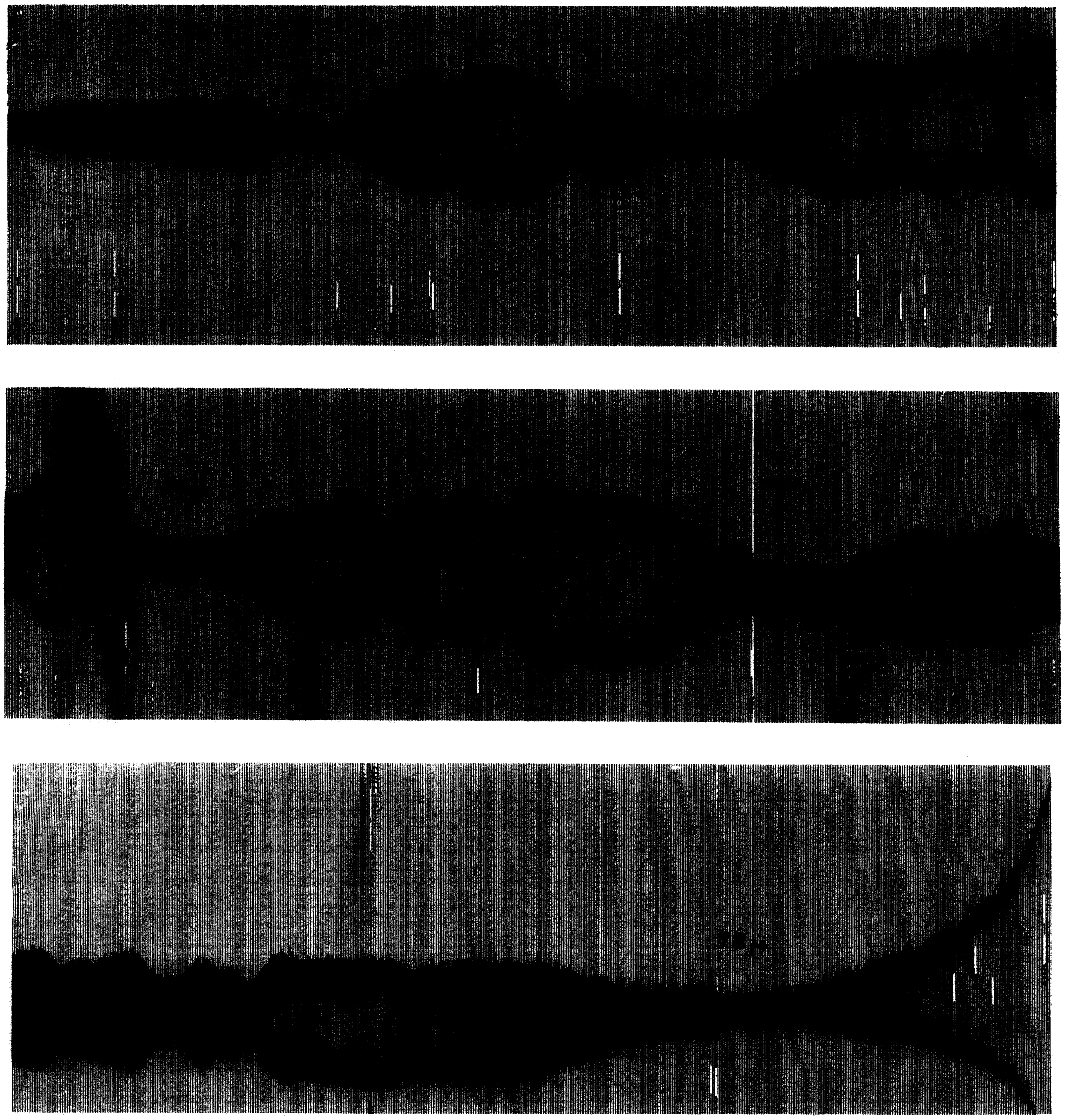

FIG. 14. The spectrum of ammonia between 40 and 75μ with a large quantity of gas in the optical path. The fine lines between the regions of strong absorption are due to transitions between excited vibrational states. With a small quantity of gas these lines would disappear and the rotational doublets would reappear, No. 7 at 72μ, No. 8 at 63μ, etc.

sufficient time had not been allowed for equilibrium conditions, as some small drift appears. There are also some other imperfections which experience would have prevented. However as first records they were very satisfactory.

The spectra are recorded on photographic paper 20×30 inches in size. Four such sheets are used to cover the region between 38 and 73μ. Starting at 73μ with slits 2 mm wide, deflections of about 200 mm are registered. This deflection is increased to over 350 mm between 62 and 54μ with the slits the same width. From here to 38μ the slit widths are 1.5 mm, with a corresponding reduction in deflection, which is finally reduced to a minimum value as 40μ is approached. This is due to the quite complete absorption by the quartz plate in this part of the spectrum

The corresponding lines, measured on the manual spectrograph and on the photographic records, may be compared as shown in Fig. 13, since they bear the same numbers. There is a very evident one-to-one relation between the two sets of data. It is customary to vary the amount of absorbing gas to give not more than 50 to 70 percent absorption for the best measurements. This was not done with the recording instrument in this test as the purity of the spectrum, obtained by using absorbing plates of quartz and paraffin, was to be tested by the completeness of absorption for the strongest lines. The results show nearly 100 percent absorption for some of the lines which indicates that the spectrum is sufficiently pure.

While the conditions were not favorable for the best resolution, as too much vapor was present, still, in one case only was a weak line not distinctly separated by the recorder, its presence being indicated however by the unsymmetrical shape of the adjacent strong line. Without doubt a smaller amount of vapor would have shown it sufficiently separate for measurement. As it is, lines 0.5 cm^{-1} apart are easily determined. Upon comparing the single values obtained from these first records with this new instrument with the mean of those obtained earlier on the manual spectrograph, it appears, as Table I shows, that the results are extremely satisfactory, in fact the largest variations are but 0.04 cm^{-1}, a quantity within the variations of individual values found in the measurements with the manual instrument.

These results show that the spectrograph has lost none of its sensitivity, accuracy of measurement, or high resolution by being turned into a self-recording vacuum instrument. It is possible to start it in the morning and by late afternoon obtain a completed record, very little attention if any having been given to it in the mean time. If time is an object and several observers are available, the spectrograph may be run continuously for 24 hours, obtaining three completed records which will extend over a spectral range of 25μ or more.

This demonstrates, therefore, the possibility of working in the far infra-red with an accuracy of measurement and with a resolving power as high as those available in the near infra-red. The advantages if any, are at the moment, in favor of the far infra-red region. This is because only the most violent disturbances affect this recording instrument, so that there is little lost time from outside influences. The tediousness of reading galvanometer deflections over long periods is removed, with the time thus saved available for other things. In fact, a new technique in infra-red spectroscopy seems in the process of formation. The days are past when an investigator worked with a spectrograph of his own design and construction, when he learned its idiosyncrasies and was the only one able to surmount them. Rather is it true, that such spectrographs as this recording instrument are well adapted for group research where many observations are to be carried on within a short time. Taking the experience with the prism

TABLE I. *Comparison of values obtained on manual and self-recording instruments. Columns headed ν contain the frequencies of the lines as obtained from the photographic records. Those headed RDGW, the mean values with the manual spectrograph.*

ν	RDGW	DIFF.	ν	RDGW	DIFF.	ν	RDGW	DIFF.
139.10	.09	+0.01	156.51	.49	+0.02	181.49	.46	+0.03
139.86	.84	+0.02	157.88	.92	+0.04	183.61	.58	+0.03
140.80	.81	−0.01	158.99	.96	+0.03	188.28	.28	+0.00
141.52	.50	+0.02	160.24	.21	+0.03	193.57	.57	+0.00
144.78	.81	−0.03	161.88	.90	−0.02	194.50	.47	+0.03
149.13	.15	−0.02	166.80	.78	+0.02	195.92	.88	+0.04
150.61	.62	−0.01	170.44	.40	+0.04	197.65	.62	+0.03
151.38	.37	+0.01	173.50	.50	+0.00			
153.55	.55	+0.00	176.15	.12	+0.03			
			177.65	.65	+0.00			
			178.58	.62	−0.04			
			179.10	.12	−0.02			

recorder as typical of such apparatus, it may be confidently expected that this new instrument will show for a long time increased possibilities as the technique of its operation is gradually mastered.

Practically a new region of the spectrum has now been thrown open for precise quantitative investigation. It is now interesting to consider what types of problems are likely to yield important information. One field that suggests itself is that of the vibration spectra of molecules containing several heavy atoms. Carbon tetrachloride, CCl_4, and chloroform, CCl_3H, might be cited as two examples of the many that exist. These molecules possess vibration frequencies some of which lie as far out as 50μ. It is true that the Raman spectra of most of these substances have been examined, but the experiments have invariably been made upon the liquid rather than upon the gas. There is always an unknown shift in position between the bands as observed in the liquid and in the gas, and for an adequate determination of the molecular force constants it is necessary to know the frequencies as precisely as possible. Moreover, in the case of symmetrical molecules, certain of the frequencies are inactive in the Raman spectrum but do appear strongly in the infra-red.

The infra-red vibration bands of gases possess one further advantage, since they show the influence of the rotation of the molecule. In the case of the heavier molecules it is doubtful if it will ever be possible to resolve the fine structure lines, but their envelope can be determined and this will often yield information concerning the moments of inertia.

A second class of vibration spectra which may well prove to be of great interest is that of crystals. Crystals of the molecular type possess vibration frequencies which are characteristic of the molecular groups forming the units of the crystal structure. These frequencies often lie in the far infra-red particularly when heavy atoms are involved in the motion, and their study will almost certainly prove to be of value.

We leave now the problems of vibrational spectra, and briefly consider the pure rotational effects. These lines, which correspond only to changes in the rotational energy of the molecule, lie exclusively in the far infra-red. The simplest spectra of this kind belong to the axially symmetrical molecules, two of whose moments of inertia are equal, $A=B$, while the third, C, is different.

The rotation lines of a symmetrical molecule form a series which to a high approximation is linear and exhibits the spacing $h/(4\pi^2A)$. The magnitude of this spacing varies from around 20 cm^{-1} for such molecules as HCl and NH_3, to 1 cm^{-1} for CH_3Cl, and to even smaller values for heavier molecules. The intensities of these lines are very small for the first members of the series, rise to a maximum and then decrease as the higher members at the shorter wave-lengths are reached. The position of maximum intensity may be shown to be roughly about $400\mu/(\Delta\nu)^{\frac{1}{2}}$ where $\Delta\nu$ is the interval between the lines measured in cm^{-1}. Thus the intense lines of the HCl and NH_3 spectra lie in the region of 90μ while those of CH_3Cl will be found near 400μ. In the latter case a calculation shows that absorption lines of measurable intensity will extend as far as 150μ. It is therefore evident that the present limit of measurements in the far infra-red with this spectrograph must be somewhat extended if these spectra are to be observed to best advantage.

As has been mentioned, the rotational lines of a symmetrical molecule form a nearly linear series. In higher approximation the lines deviate somewhat from linearity and moreover the higher members of the rotation series may be expected to split apart and show a fine structure. Both these effects are due to the centrifugal force stretching the molecule and are a measure of the molecular force constants. Calculations have shown that this fine structure of the rotation lines should be observable in the case of NH_3 and measurements are to be made in the near future. In passing, it might be said that the ammonia spectrum (Fig. 14) in the far infra-red has many features which are of great interest to theoretical physicists. Each of the rotation lines appears as a doublet as shown in Fig. 2. This doubling is caused by the double minimum nature of the potential function and its accurate determination leads to a knowledge of the molecular dimensions. A second point indicated by theoretical considerations is that in addition to, and between, the primary series of rotation lines there should appear other, but much fainter, ones which are to be associated with transitions between certain of the excited vibrational states of the molecule. A preliminary run using a path length of 500 cm and a pressure of 5 cm has indeed shown that these lines are present, Fig. 14, but traces of water vapor contained in the anhydrous ammonia have somewhat interfered with their measurement. This work is to be repeated under more favorable conditions.

The rotational spectrum of asymmetrical molecules, none of whose moments of inertia are equal, presents a highly complicated pattern as may be seen in the case of water vapor. Nevertheless, the quantum theory of the asymmetrical rotator is adequate for its interpretation. It would be very desirable to investigate other examples of asymmetrical molecules such as H_2S and H_2Se which together with D_2O, will find an early place on the proposed program.

This brief survey of the problems which await us in the far infra-red is far from complete. One thing seems to be common to all of them: The most interesting features—the envelopes of vibration rotation bands, the fine structure of the rotation lines, the doubling of the NH_3 lines and the rotation spectra of asymmetrical molecules—all demand a high degree of resolving power. An instrument with but a small fraction of the resolution of the one just described would be completely inadequate on all these points. It seems probable that future investigations, whatever they are, will continue to require such detail.

A development extending over a period of years as this one has, inevitably adapts to its own purposes the contributions of many people. I wish to make at this point full acknowledgment of the assistance which the work of other investigators in this field has been to me. Particularly am I indebted to Professor F. Paschen who introduced me, in his laboratory at Tübingen, into a domain of, for me, ever increasing interest, that of infra-red spectroscopy; and to my colleagues at Michigan who have been associated with me in this work for so many years. They will join me in expressing our common indebtedness to the staff of our instrument shop, who have always provided us with such exceptional equipment for our researches.

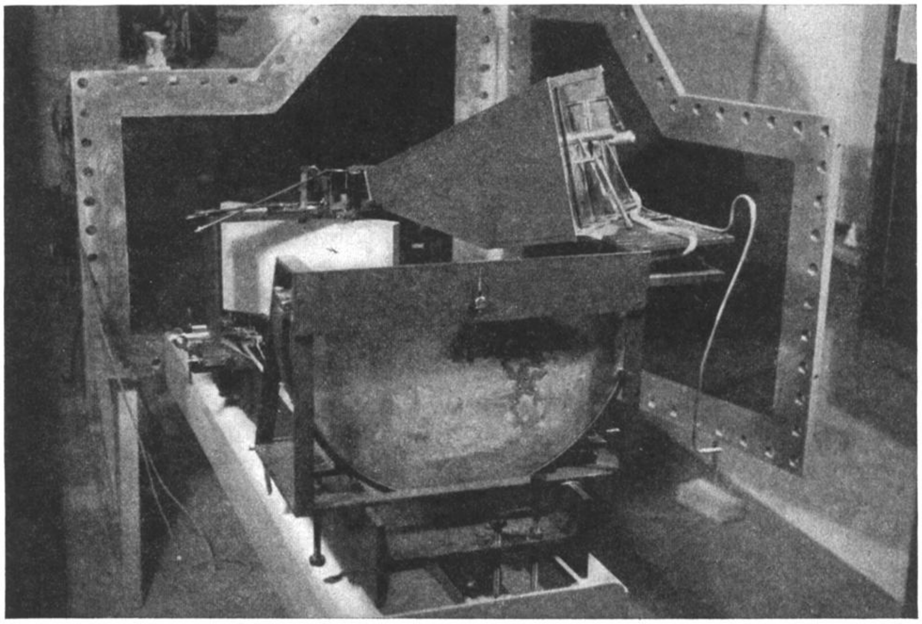

FIG. 10. Spectrograph viewed from the rear, ready to be rolled into the vacuum case.

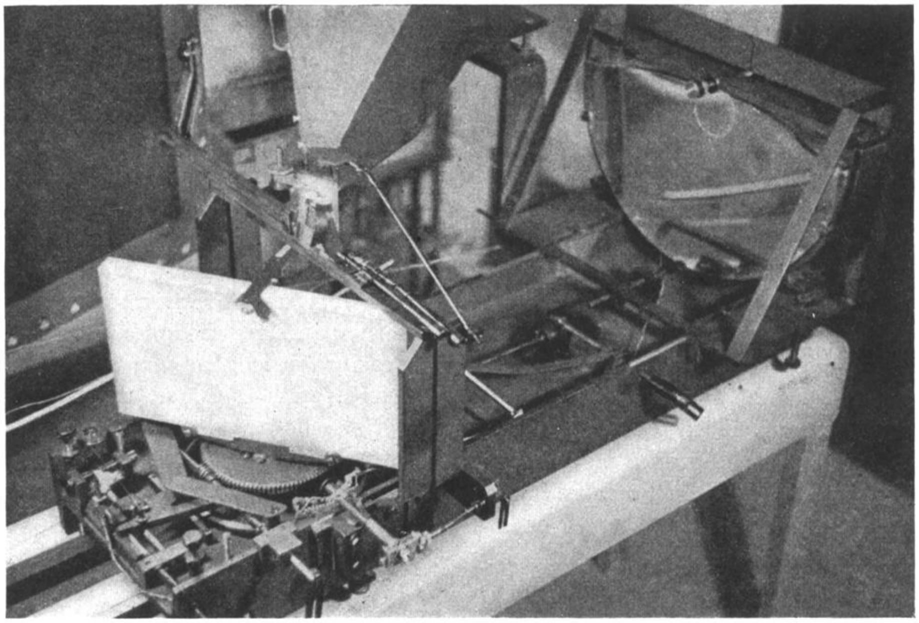

FIG. 11. Spectrograph viewed from the front.

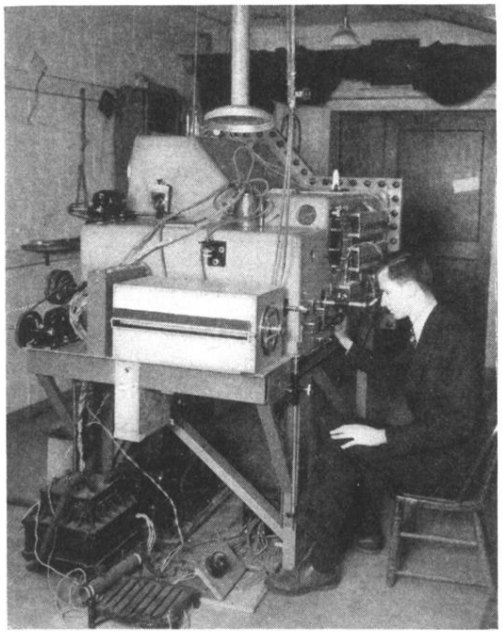

FIG. 12. View of spectrograph case showing outside attachments.

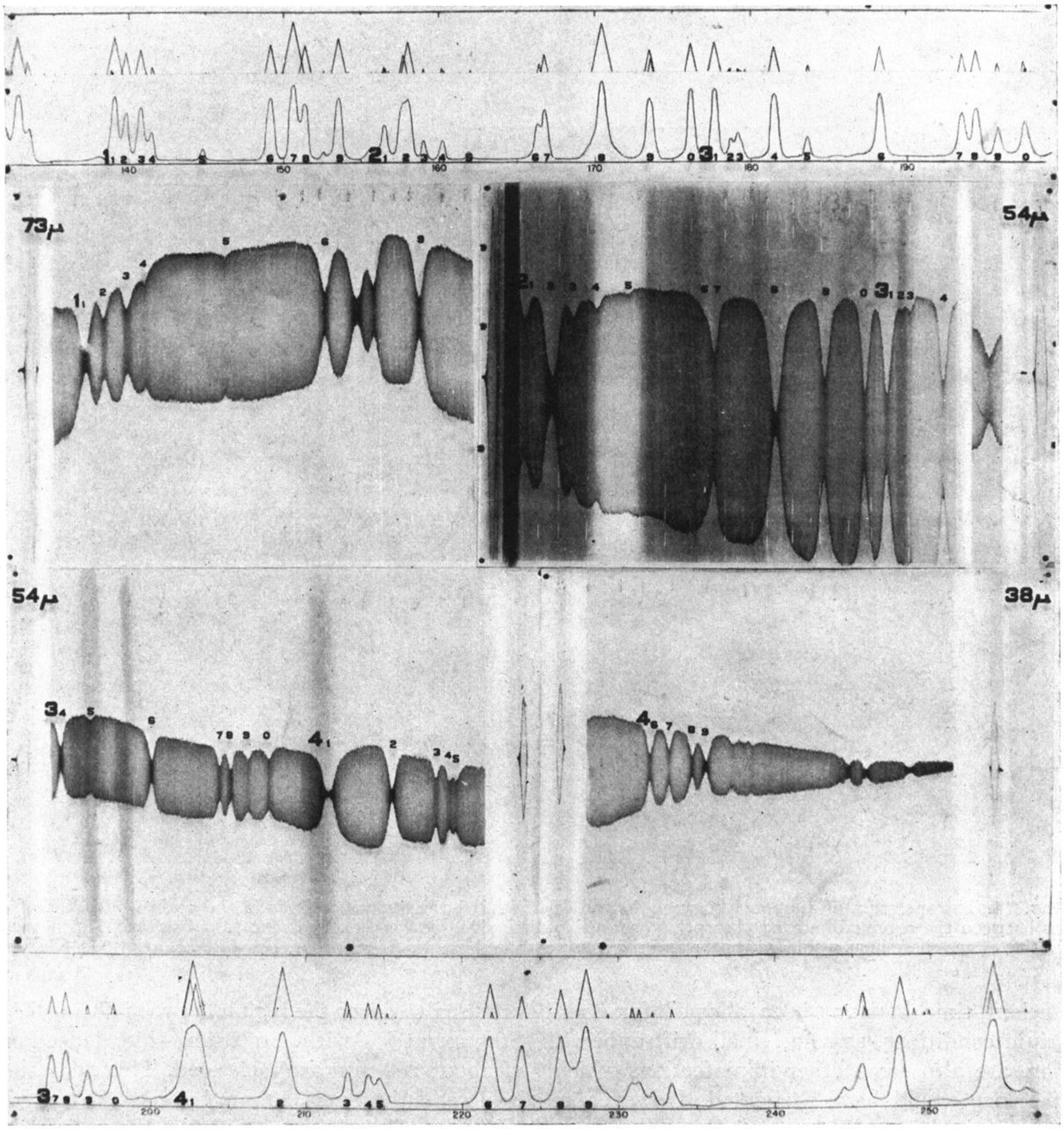

FIG. 13. Four photographically recorded records of the rotational spectrum of water vapor between 75 and 40μ. Above and below are plotted the mean wave-lengths of the lines obtained with the manual spectrograph. The corresponding lines bear the same numbers.

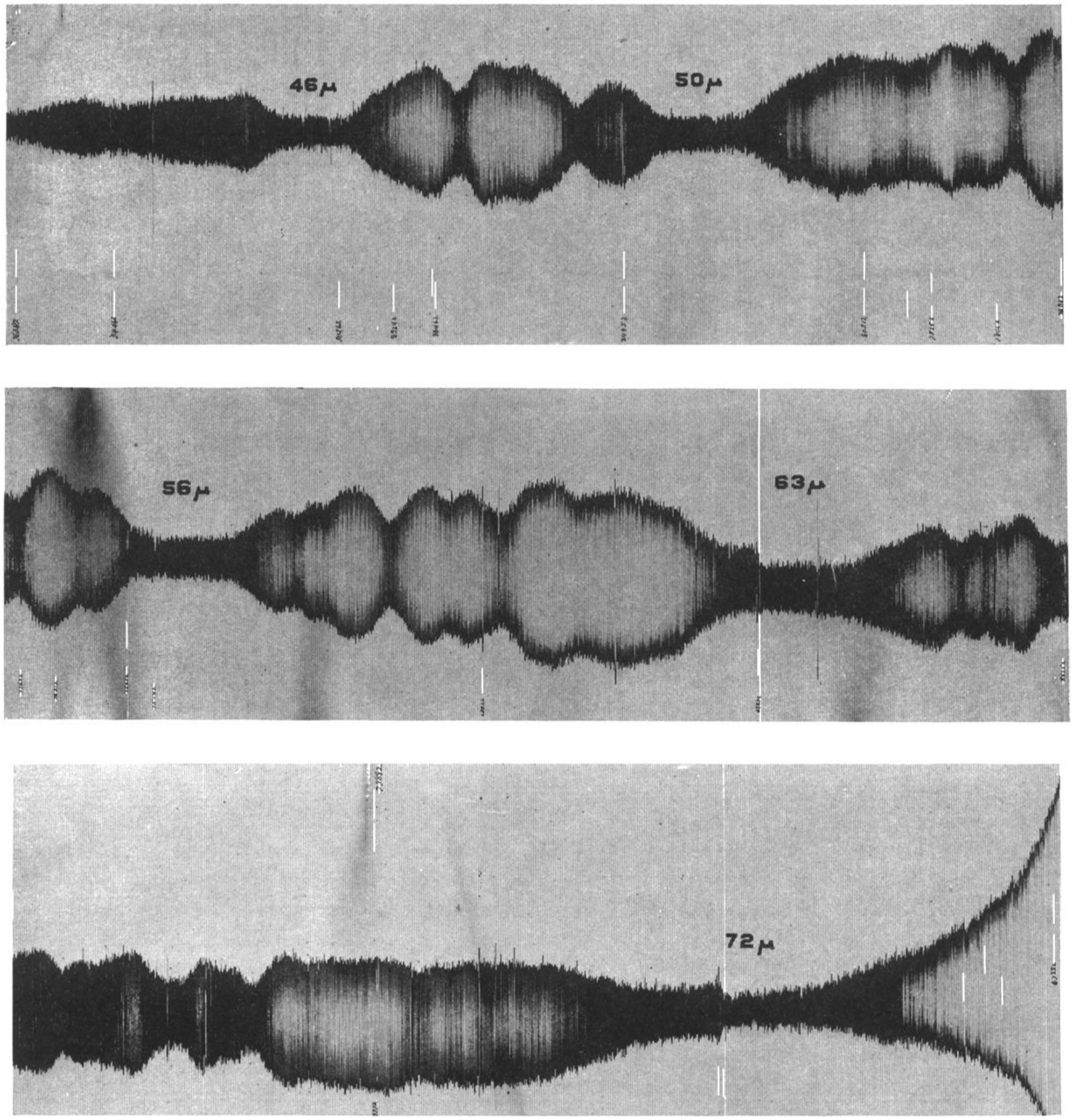

FIG. 14. The spectrum of ammonia between 40 and 75μ with a large quantity of gas in the optical path. The fine lines between the regions of strong absorption are due to transitions between excited vibrational states. With a small quantity of gas these lines would disappear and the rotational doublets would reappear, No. 7 at 72μ, No. 8 at 63μ, etc.

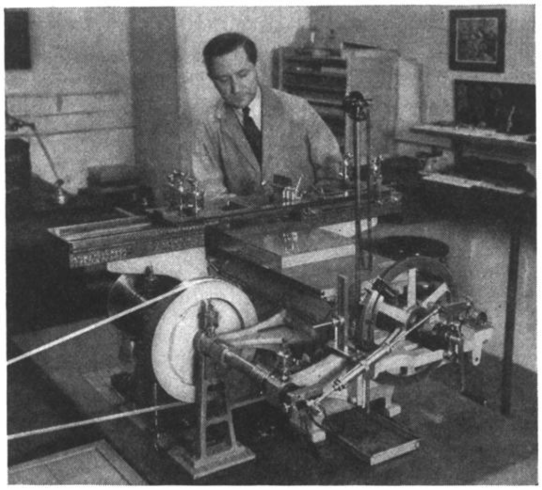

FIG. 4. The Michigan ruling engine.

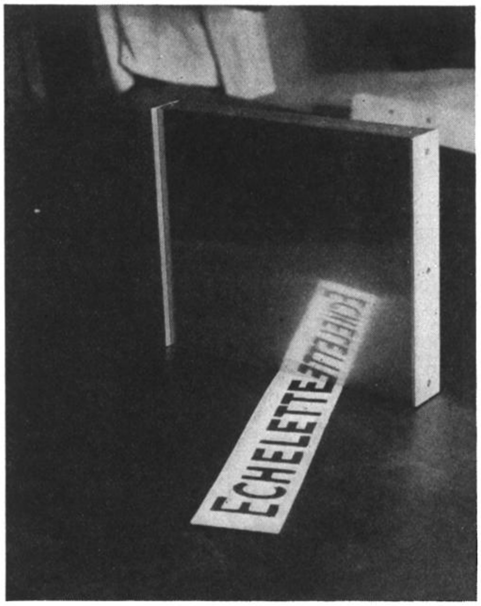

FIG. 5. The grooves of an echelette grating have plane sides, one wide, inclined at about 25° to the face of the grating, and one narrow, nearly perpendicular to the face. In Fig. 5, the paper strip is normal to the planes of the wide or working sides of the grooves.

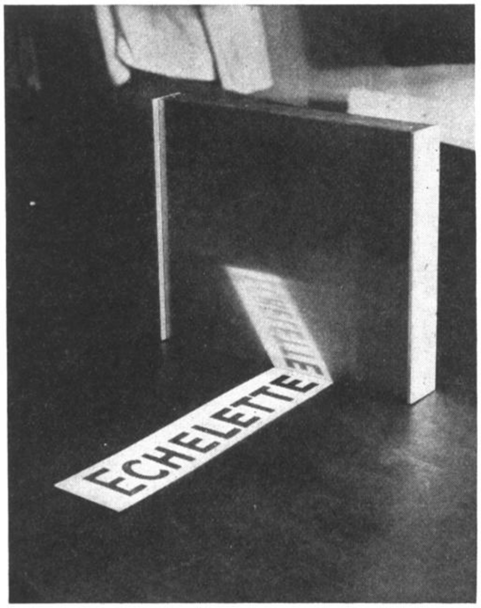

FIG. 6. The paper strip is normal to the surface of the grating.