Infra-Red Spectra—Observation and Uses

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A nontechnical description is presented of methods of observation now in general use in
infra-red spectroscopy, together with some typical examples of their use.

INFRA–RED radiation, sometimes referred to as heat radiation, comprises that region of the general radiation field which lies beyond the red end of the visible spectrum, but has not yet been extended to reach the shortest of the waves generated by purely electrical methods. This places its shortest wave-lengths at about 0.7μ while the longest measured to date are around 500μ or $\frac{1}{2}$ mm. Photographic plates are now sensitive to 1.5μ so that the spectral region of wave-lengths shorter than this is being gradually included in the field of photographic spectroscopy. In this paper we will consider those radiations lying beyond 1.5μ, which cannot be investigated by the usual photographic methods.

Such radiation has to rely for its measurement first upon the conversion of the radiant energy into heat energy, and second, the conversion of this heat energy into electrical and mechanical energy. The first of these conversions, under favorable conditions, may be quite efficient, but the second conversion is an extremely inefficient one. This is not because the proper experimental means for an efficient conversion have not yet been applied, but rather because the same inefficiency holds here as necessarily with all heat engines, of which the thermopile-galvanometer combination is one.

Since its first discovery in 1800 by Sir William Herschel, this spectroscopic region has attracted its investigators, but their number has always been small in comparison to that of those engaged in developing the photographic region or the field of x-rays. Progress has thus been correspondingly slow because of the resulting lack of concentrated effort in infra-red research. A further result of the small personnel has been that the instrument makers not finding sufficient market for infra-red equipment have not contributed so appreciably to the advancement of

this type of spectroscopy as to the other fields. The infra-red spectroscopist has thus had to go his own way with comparatively little inspiration from fellow workers or help from instrument makers. In spite of these drawbacks, and the difficulties inherent in the subject itself, steady progress has been made from the first and today infra-red spectroscopy is contributing its proper share to the development of pure science and promises to become a powerful tool in industrial research.

Early investigators naturally concerned themselves with the devising of the equipment and procedures necessary to penetrate the new region. When quantitative measurements became possible, among other problems the radiation from heated surfaces was studied resulting in the production of the blackbody radiation, the explanation of whose laws, determined empirically, led to the first formulation of the quantum theory. When the time came to explain atomic spectra in terms of modern atomic theory, many of the crucial tests were supplied by infra-red measurements of the emission spectra of the elements. The accuracy and sensitivity of these measurements, if not equal to those of the data obtained photographically, were still sufficiently good to serve this purpose. As the problems of atomic spectra were approaching solution molecular spectra came on the field. Here infra-red spectroscopy has shown its greatest power to date as an instrument of research. With the gradual but continuous improvement of equipment and techniques employed, this type of spectroscopy is supreme in the field of band spectra not involving electronic transitions.

Starting with simple molecules where the bands were few and isolated and where higher resolution simply accentuated the structure of the bands, the work was gradually extended

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to more and more complex molecules, such as those of organic chemistry. The spectra of these latter molecules are very complicated as would be expected considering the many kinds of vibrations and rotations possible within such complicated systems. There are at present no hopes of interpreting their spectra by the methods so successful with the spectra of the simpler molecules; further resolution but discovers more complexities of these spectra. However, it has been observed particularly with organic substances that certain lines are very often present with but small variations in their measured wave-lengths and frequencies, as one goes from one compound to another, this being true whether the material be in the solid, liquid, or vapor phase. In these compounds certain combinations of atoms are also of frequent occurrence such as the $O - H$, $C - H$ and $C - CH_3$ groups. A correlation between these atomic combinations and the observed absorption lines just described has been made. Stating the idea very concretely "every organic radical gives rise to a characteristic series of bands, its characteristic frequencies being practically unaffected by other groups present in the same molecule or in neighboring molecules."[1] How far this idea may be profitably carried, only experience can decide. Certain of its relations, however, do appear well established and have been used effectively. Table I contains a number of such groups and their assigned frequencies.

Returning to the problem of infra-red band spectra and the use made of these spectra in the development of the theory of molecular structure, it will be evident that the more completely a spectrum may be resolved and measured the better the chances that an interpretation of the data in terms of molecular structure may be found. Beginning with the simplest molecules, diatomic, and choosing such as would have spectra of open structure, infra-red investigators have gradually proceeded from such simple molecules as HCl with a fine structure separation of 20 cm^{-1} to such complicated molecules as methyl alcohol, and to spectra where the fine structure separation is not more than 1 cm^{-1}. This progress has been achieved by appreciable improvements in apparatus and experimental techniques together with a simultaneous and

corresponding increase in the power of the theoretical methods employed in the analyses. The spectroscopic arrangement[2] which the writer adopted in 1918 for the use of his students was an adaptation of that used by Langly in his measurement of the infra-red spectrum of the sun in 1880. This arrangement shown in Fig. 1, which brought the large dispersion and high resolution furnished by gratings into play in the measurement of molecular spectra has since been almost exclusively used as being particularly well adapted for work in this type of spectroscopy. It is in fact a combination of two spectrographs, a prism instrument of low dispersion, and a grating instrument of high dispersion. The function of the first is to present to the slit of the second radiation free from higher orders. The prism has accordingly a small refracting angle and its spectrum is moved across the entrance slit of the grating instrument by steps as the measurements proceed. For the far infra-red beyond 25μ where no prism material is transparent, the spectrograph,[3] Fig. 2, is limited to the grating instrument, and absorbing screens and reflecting surfaces are used to obtain pure spectra.

At present it is possible to separate sharp lines in both the near and far infra-red which are somewhat less than 0.5 cm^{-1} apart. From this it is apparent that better than this should be possible in the near infra-red; namely, in the region between 1 and 20μ where the available energy is much greater and other experimental conditions are generally more favorable.* The

TABLE I.

$\nu(C - H) \lesssim 3000$ cm^{-1}	$\nu(C - C) \lesssim 900$
$\nu(O - H) \lesssim 3300$	$\delta(CH_2) \lesssim 1440$
$\nu(C = C) \lesssim 1500-1800$	$\nu(CCl) \lesssim 700$
$\nu(C - O) \lesssim 1500-1800$	$\delta(CO_2) \lesssim 667$

chief improvements in recent years may be listed as follows: (1) The introduction of the vacuum thermopile. (2) The use of amplifiers possessing amplifying factors of from 50 to 200 times. (3) The use of echelette gratings, which

* Since the above was written a letter from H. H. Nielsen informs me that he is measuring lines of water vapor from 0.25^{-1} cm to 0.3^{-1} cm apart in the region 1.5μ to 7μ.

localize the energy very largely in a narrow spectral region. (4) Improvement in the optics employed with the result that the spectral image at the emergent slit shows less distortion than formerly. (5) The increased use of vacuum spectrographs, which prevents the loss of energy by the absorption of the water vapor and carbon dioxide of the air. No satisfactory improvement in the sources has been found though the larger gratings, up to 10 by 20 inches in ruled surface, have increased the available energy many times.

In the set-up shown in Fig. 1 the source L is usually, for work in the near infra-red, either a Nernst glower or a glowbar heated to a high temperature, 800°C or more, by a suitable current. For work in the far infra-red the best source is the white-hot surface of a gas mantle, the reason being that this source is deficient in those radiations of short wave-length which comprise the impurities most difficult to remove by absorbing screens and reflecting surfaces.

Fig. 1. Prism-grating spectrograph.

Unfortunately having to burn in the open air this source can be used in a very limited number of instances only. Generally a glowbar, a commercial heater unit, or platinum ribbon covered by thin layers of various materials are the most convenient, though at best form but unsatisfactory sources. Covered by powdered gas mantle material or some of the oxides composing these mantles, a better radiating surface is formed than the blank platinum surface would furnish, but not one possessing the characteristic radiation which makes the gas mantle, when heated by burning gas, so advantageous a source for far infra-red work. While hot sources are quite satisfactory for the near infra-red region, it may be possible some time to replace them to advantage if a source directly transforming electrical energy into the radiation of the long
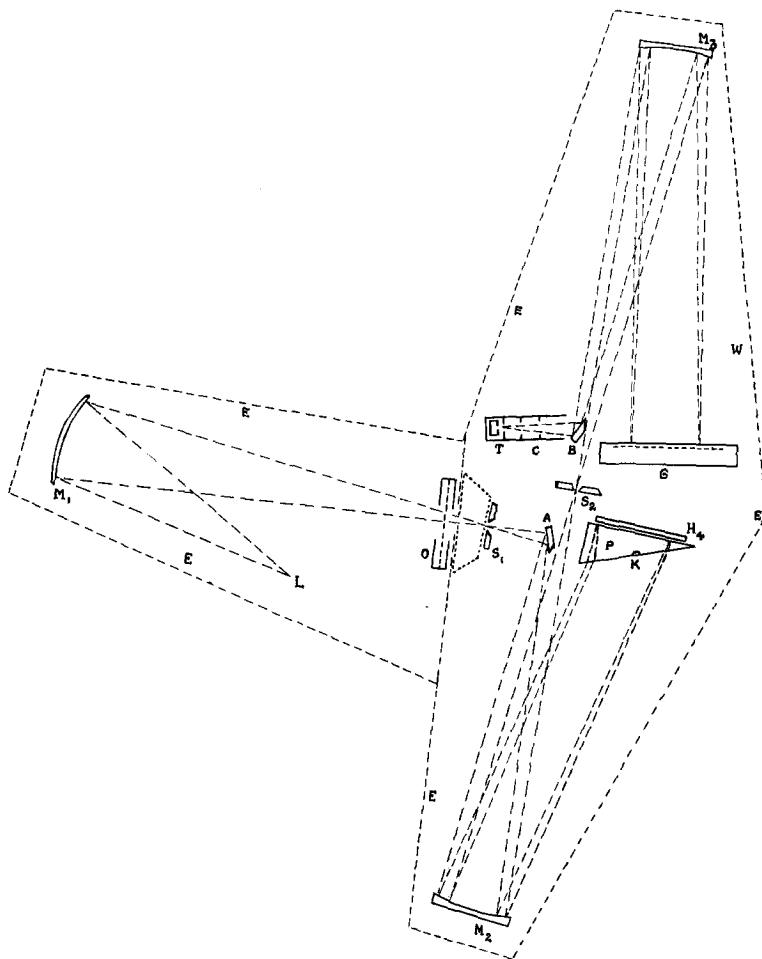
wave-length region could be devised. The reader will perceive that the source of radiation is no problem for the near infra-red region but is a vital one in the far region. An illustration will explain the situation. By using the laws of black-body radiation as being sufficiently applicable to the radiation of our sources for this purpose, it will be found that the radiation at 100μ in a given narrow spectral region is $\frac{1}{16}$ that in a corresponding region at 50μ and at 200μ, but $1/256$ that at 50μ. The reverse would be true were it possible to get a purely electrical source to emit measurable radiation at 50μ. The longer radiations would be progressively more easy to produce.

The slits S_1 and S_2 which pass the radiation into and out of the grating instrument, Fig. 2, should be adjustable in width, without changing

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the constant of the spectrograph at the same time. For investigations where maximum supply of energy is a requisite long slits, possibly 2 inches, may have to be used. Here the optics of the spectrograph will produce a curvature in the slit image. As a linear thermopile is easiest made, the emergent slit should be straight. If the curvature is a function of the deviation produced by the grating, then the entrance slit must be curved and the curvature adjustable. When plenty of energy for the work is available and short slits are adequate, no questions of curvature will arise. This refinement need not be considered for the prism instrument preceding the grating.

Coming to the grating, what are the considerations which determine its choice? Generally speaking, greater dispersion and higher resolution has characterized the progress in infra-red spectroscopy; that is, a longer spectrum and a narrower strip of it, used to activate the thermopile. This process, which diminishes the energy reaching the thermopile, may be in part compensated by using larger gratings. In fact for the near infra-red, gratings now have ruled surfaces of 7×9 inches where twenty years ago the ruled surfaces were expressed in terms of about the same number of centimeters.

The first gratings used in this division of spectroscopy were gratings ruled for the photographic field. A grating with 15,000 lines per inch permits measurements to 3μ, while a grating with 5000 lines per inch would be usable to still longer wave-length regions. But these gratings generally produced a multiplicity of spectra of different orders both to the right and to the left of the undeviated image, into which image also a good deal of energy went. This dissipation of the available energy into many spectra made working with gratings much more difficult than with prisms where all the energy of a given frequency is conserved in a narrow strip of a single spectrum. This disability of the photographic gratings has been to a very appreciable extent overcome by the use of echelette gratings,[4] which approach prisms in their ability to locate radiation of a given frequency in a single spectral order. This result is achieved by ruling the grating on a soft surface, the shape of the ruling tool being such that the lines have the form of

shallow V-shaped grooves, one side wide and one narrow. The narrow one, nearly normal to the grating surface is ineffective, the wider one, inclined at about 24° to the surface of the grating, is the working face of the groove. By loading the ruling tool properly the grooves, for the finer gratings, are made just deep enough to eliminate practically all of the original surface of the grating. There is accordingly very little energy reflected back into the undeviated image. Gratings with the working faces of the grooves inclined at about 24° to the grating face and with 1200 lines per inch throw the radiation at 18μ very strongly into a single first-order spectrum. Spectral regions at each side of 18μ are not so strongly localized but still permit the spectrum between 15μ and 25μ to be measured. Similarly a grating with 900 lines per inch may be made to function well on each side of 30μ, a 600-line grating around 50μ, a 360-line one around 90μ, a 133-one at 110μ and one 87.8 lines per inch at 140μ. Thus to measure the spectrum between 18 and 150μ it has required the use of six gratings, all of them having ruled surfaces of 10×20 inches except perhaps the 1200 line grating where a surface of 9×9 inches would be sufficient. Similarly in the near infra-red a collection ranging from a maximum ruling of 15,000 lines per inch to 1200 lines is required.

From the foregoing description of the workings of echelette gratings it might appear that they were as effective as prisms. This is far from being the case however. Superposed upon the first-order spectra whose conservation by the echelette grating has been stressed are also similar concentrations of all the higher orders corresponding to the first order. For the near infra-red, where transparent materials are available for prisms, the separation of these higher
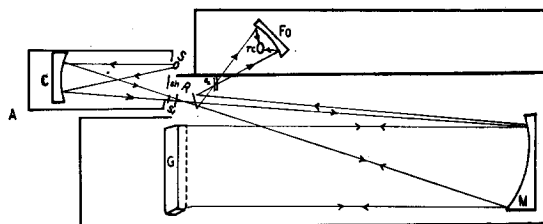

Fig. 2. Grating spectrograph for far infra-red (side view). S, source; A, absorption cell; M, half-parabolic mirror; G, echelette grating; TC, thermocouple.
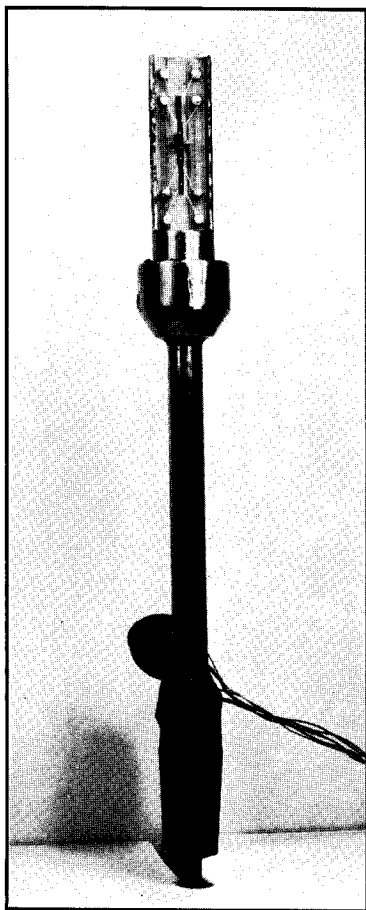
FIG. 3. Thermopile after Weyrich.

orders presents no difficulty since the prism instrument is adjusted to present to the entrance slit of the grating spectrograph only the first order of the radiation under examination. For the far region this overlapping of higher orders constitutes a very serious difficulty. So far these orders are eliminated only by absorbing screens and suitable reflecting surfaces. At each absorption and reflection some of the first-order radiation under examination is lost along with the radiation of shorter wave-length which it is thus sought to eliminate. When sufficient purity has been attained by these methods only a small fraction of the original first-order radiation may have survived. Better methods of purifying the spectrum are urgently needed.

The large number of echelette gratings required if an extended spectral region is to be

covered constitutes a decided handicap to the use of these gratings. However since work in this field has been one of the major research interests at Michigan it appeared desirable to be in a position to rule as many echelette gratings as might be necessary. A ruling engine was accordingly built. The gratings now being ruled on this ruling machine, judged by the quality of the results obtained in all the investigations carried on with them both in this country and abroad are quite adequate to meet the demands so far made upon them. No comprehensive study of the engine or of the gratings ruled by it has been made though that is desirable and may be necessary should the time arrive when the gratings become the weak member of the combination which constitutes the infra-red spectrograph.

Of the early gratings which were successful, one was ruled on a surface of a copper nickel alloy and several on aluminum surfaces. Now pure tin is used where the lines per inch number more than 2400 per inch and solder when coarser gratings are ruled. The grooves of the finer gratings are pressed out by carefully shaped diamond tools but with the coarser gratings it has been found necessary to remove the material and a cutting tool of steel is used. The solder surfaces have maintained their brightness for the length of time which has elapsed since they were first used, that is about 6 years. With the methods of evaporating films of noncorroding metals, such as aluminum or chromium, becoming constantly more accessible these solder surfaces may shortly be protected by such films. Moreover, the fixing of thin solder surfaces upon the blanks of aluminum alloy presents difficulties which also may be avoided by the evaporation of soft metals upon optically flat glass surfaces. The engine will rule gratings as fine as 14,400 lines per inch. The coarsest grating ruled so far has 25 lines per inch. The engine can undoubtedly be used to rule laminary gratings which have some definite advantages for use in the far infrared.

Returning to Fig. 1. While care was taken to have the angle between the axes of the beams incident on the concave mirrors M_2 and M_3 and the axes of the mirrors as small as possible still an

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appreciable angle exists which results in some distortion of the image formed at the exit slit with a corresponding decrease in resolution. From Fig. 2 it is evident that if the parabolic mirror M were a complete mirror and the beam through the entrance slit had sufficient aperture completely to fill the mirror the axes of the beam and mirror could be made to coincide with a resulting minimum of distortion of the image formed by the mirror upon the emergent slit. This method of half-mirrors used here for some twenty years presents decided points of advantage in reducing aberration. More recently[5] the same result has been obtained by employing two parabolic mirrors reinforced by two plane mirrors mounted immediately adjacent to the slits with apertures at their centers to pass the radiations proceeding through the slits. In any case, for maximum resolution, the image distortion should be reduced to a minimum. Resolution may also be increased by lengthening the focal length of the collimating mirror or mirrors. These have been increased in the course of time from about 20 cm to one meter or more in both the near infra-red and far infra-red spectrographs.

The emergent slit S_2, Fig. 2, is made one of the foci of the elliptical mirror behind the thermopile while the thermopile surface is at the other focus. This use of elliptical mirrors has resulted in very sharp images of the emergent slit upon the thermopile receivers, reduced in size in the ratio of about four to one.

There remains to be described the thermopile which at the present time is the device most frequently used to measure the energy of the radiation in the different parts of the spectrum. The instrument is outwardly simple enough, but a good thermopile represents not only exceptional skill in the manipulation of the very small parts composing the pile but also a most careful consideration of all the numerous factors which go into the design of this instrument. Anyone seriously interested should consult one or more of the authoritative articles on the subject.[6]

Figure 3 shows a thermopile and its mounting. The receivers, upon which the radiation passing the emergent slit of the spectrometer is focused, are shown—four in number—forming a linear pile 18 mm long and 0.8 mm wide—a size de-

termined by the operating conditions for the far infra-red. Soldered to the backs of each of these receivers, which are of very thin tin, is the thermojunction of the couple which also supports it. The cold ends of the couple are soldered to the copper plugs mounted in the lucite form above which the pile is mounted. The thermopile wires are of Hutchin's alloy (95 percent $Bi - 5$ percent Sn and 97 percent $Bi - 3$ percent Sb). Copper leads, soldered to the other ends of these plugs pass down the metal tube and out of a side tube near the bottom. At this point these leads are carefully cemented in the side tube and, once tight, remain so. This vertical tube, which supports the pile, ends in a ground joint which makes a vacuum seal with the copper tube leading to the pump. A metal cap, with a window of proper size, slips over the pile in its containing tube, which is half cut away for the length of the pile. The cap extends into a groove in the enlarged part and the joint is made vacuum tight with Apiezon wax. Several such caps, one with a window of KBr, one of hard paraffin, and a third of crystalline quartz are provided. The ground joint union at the end also permits the exchange of one thermopile for another with a different absorbing material on the receivers. These arrangements have been found very advantageous when long spectral regions are to be covered as they permit using the best window material and

FIG. 4. The far infra-red spectrum of D_2O between 31μ and 38μ.

receiving surfaces at each part of the spectrum. A pair of wires from each couple permits joining the couples in any desired way before being soldered to the galvanometer leads. In the present case the two lower couples are joined in series in

opposition to the two upper couples in series. This method aids in preventing drifts when the shutter is built to illuminate first the upper pair, then the lower pair, as it operates. Such a couple, if properly made, will gain in sensitivity 3 to 10 times when evacuated to a pressure of 10^{-5} mm of mercury. This one will give an amplified galvanometer deflection of 400 mm, when 0.036 erg/sec. falls upon the receivers; the period of the galvanometer being 16 sec.

With the prism grating spectrometer, higher orders are eliminated by the prism but in the far infra-red various combinations of absorbing screens and reflecting surfaces have to be used to obtain pure radiation. The thermopile receivers are covered with absorbing material which varies with the part of the spectrum under examination: bismuth black in the near infra-red and Aquadag (graphite) or powdered glass for the far region. An ideal coating would be a material 100 percent absorbing in the region under investigation, and reflecting in other regions. The thermopile windows act as filters as well; the paraffin absorbs the shorter waves below 20μ more strongly than the longer ones. The crystalline quartz windows absorb between 4μ and 50μ. Filters made of films covered with antimony black of the right coarseness are opaque for the near infra-red but become good transmitters beyond 50μ.

The mirror, R (Fig. 2), may be replaced by *reststrahlen* plates of different materials which reflect copiously in the region under examination,
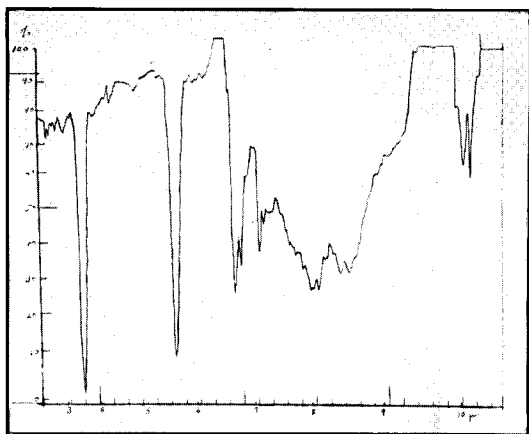

FIG. 5. The Hardy recording spectrophotometer, registering as ordinates the percentages of transmission. Region 2.5μ to 10.5μ.

and poorly elsewhere. A series of plates whose regions of reflection change by small steps between 20 and 100 are provided. Finally the shutter, which passes the radiation from the source intermittently through the entrance slit, may be transparent to the radiation suppressed and opaque to the radiation under examination— in which case the current pulses to the galvanometer are due primarily to the interruptions of the latter radiation. It has been found possible by suitable combinations of filters and reflecting surfaces to obtain sufficiently pure radiation between 20 and 140μ.

The cable connecting the thermopile with a high sensitivity galvanometer should be well shielded within a metal tube and if high frequency oscillations of considerable power are in operation in the building it is well to connect across the cable, where it is attached to the couple terminals, a high frequency choke in order that, if the cable picks up high frequency pulses they will not run through the couple, there developing temperature differences through the Peltier effect.

The deflections of the galvanometer connected to the pile are at most small and it has become customary to amplify them to as much as 200 or more times. In as much as all mechanical disturbance in the galvanometer as well as transient electrical and magnetic effects picked up by the thermopile circuit are also amplified it is evident that high amplification is only justified if all extraneous sources of disturbance have been very strictly prevented. Mechanical disturbances which cause movements in the galvanometer coils may be eliminated quite completely by various shock absorbing devices. Air currents about the coils are not entirely prevented as galvanometers are usually housed but can be eliminated by enclosing the instrument in a vacuum case or even an air-tight one if temperature differences can be avoided.

When all outside disturbances have been eliminated there still remain the Brownian movement effects of the galvanometer coil and similar effects of an electrical nature in the thermocouple circuits which cannot be eliminated. From this it appears that currents from the thermopile which cause galvanometer deflections of the same order of magnitude as the Brownian movement effects cannot be amplified to advantage. These effects

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set a definite limit to the minuteness of the infra-red energy which may be measured by these methods. For the circuit employed in the spectrograph of Fig. 2 the r.m.s. deflection of the light beam at the camera drum due to Brownian movement of the galvanometer connected to the thermocouple is about 4 mm. When the deflection is 400 mm the mean error in the deflection will be about 1 percent.

There are a number of well-known amplifiers used to increase deflections. For recording instruments it is very important that there be no drift. As the instrument of Fig. 2 is a recording instrument the amplifier which amplifies 200 or more times is a periodic one,[7] that is it amplifies only impulses applied to it of a definite period. By operating a shutter at the entrance slit at this same period, 16 sec., only the galvanometer deflections arising from the thermopile currents are amplified, and drifts are quite completely eliminated. The advantages from amplification do not lie in larger deflections simply. They permit the use of the more stable D'Arsonval type of galvanometer which is quite free from magnetic disturbances.

Both types of spectrographs shown in Figs. 1 and 2 require very accurately made cones and calibrated circles otherwise the errors in determining the position of the grating may result in larger errors of measurement than would arise from all of the other sources of variation.

Infra-red observations by telescope and scale or by other similar devices for reading galvanometer deflections by eye are very tedious operations and for some time recording methods have been making their appearance. A good recorder usually reduces very materially the actual time required to measure a given spectral region. Moreover the accuracy with which lines may be measured are not unfavorably affected. Direct comparison of measurements of the rotational lines of water vapor over an appreciable spectral range made by a manual spectrometer and by a recording one showed an average deviation in values of 0.035 cm^{-1} with a maximum deviation of 0.07 cm^{-1}. The measurements were not only made at different times by different observers but upon different spectrographs with different gratings. With the recording instrument just mentioned weaker lines are
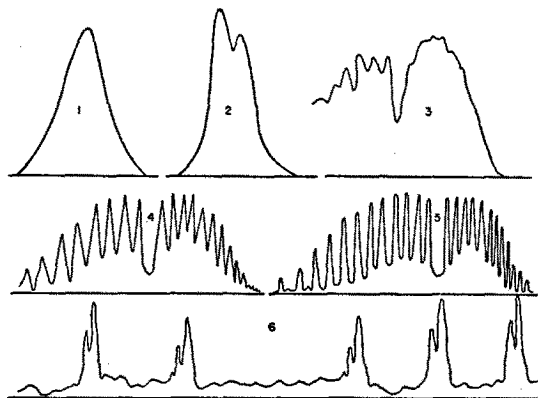

FIG. 6. The band of HCL at 3.5μ. 1, Angstrom and Palmer, 1893, width of slits 4000A. 2, Burmeister, 1914, slits 400A. 3, von Bahr, 1914, slits 100A. 4, Brinsmade and Kemble, 1917, slits 70A. 5, Randall and Imes, 1919, slits 39A. 6, Meyer and Levin, 1929, slits 7.5A.

regularly recorded that would usually be passed over in manual observation. Not only is the actual time in covering a given spectral region less but it may be possible to make the recording so automatic that, having once been started, no further attention will be required, the operator returning later at his convenience, the mechanism having automatically stopped the record upon its conclusion. This saving of time is an important factor and is often sufficient to permit the operator to measure entirely one record while a second one is being made. In Fig. 4 is recorded the rotational spectrum of D_2O between 31μ and 38μ.[8] While this particular record was run in the slowest time of operation, namely, eight hours, it is evident that no drifts have adversely affected this recording. Usually sufficiently satisfactory records may be obtained in much shorter periods, namely a little over two hours. In this case, if one record was being measured while another was recording, the fifty lines between 31 and 38μ would be completely measured in less than three hours.

The record of Fig. 4 is one giving energy distribution only and if one wished percentages of absorption in addition to wave-lengths it would have been necessary to run on this same record immediately before or after this record was made, a second record with no absorbing vapor in the optical path. The time required for this together with the measurements necessary to obtain percentages of absorption would be about
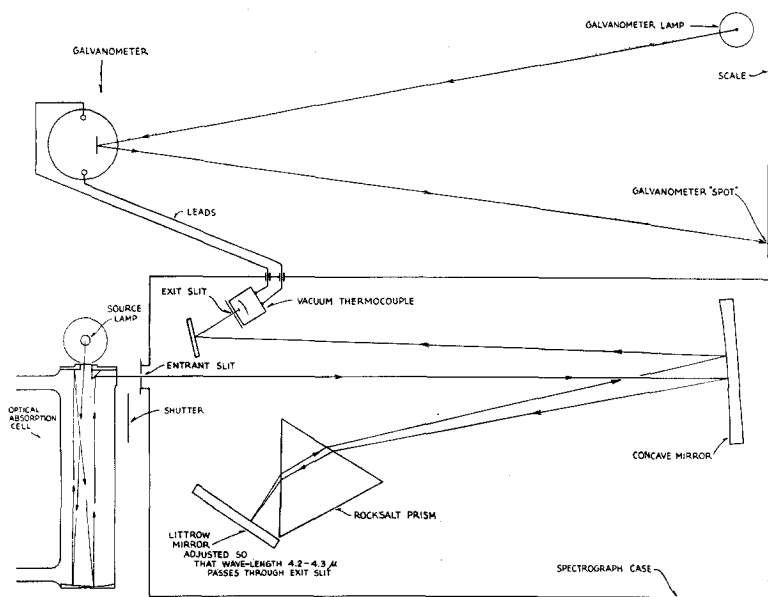
FIG. 7. McAllister recording spectrograph used in investigations in photosynthesis.

close as 0.35 cm^{-1} have been sufficiently resolved for measurement.

In the far infra-red an investigation of the rotational spectrum of water vapor shows a similar improvement. The region is near 100μ. In 1924 the grating used had 25.4 lines per inch with a total of 71 lines. In 1939 the grating had 360 lines per inch and a total of 7200 lines. In 1924 the effective slit width was 10 cm^{-1}, in 1937 it was 0.22 cm^{-1}. As a result of this higher sensitivity and correspondingly greater resolution, the rotation spectrum of heavy water,[8] D_2O, has recently been measured with the result that some 210 absorption lines have been measured with an average uncertainty in their frequencies of around 0.03 cm^{-1}. It speaks well for the advance in theoretical physics that the majority of these lines have been accounted for, some 110 distinct rotational energy levels being determined.

As the difficulty of obtaining atoms of sufficiently simple structure and open spectra for satisfactory analysis increases, infra-red investigators are turning more and more to the field of organic chemistry where a purely empirical development of great significance is taking place, some results of which have been tabulated in Table I. These results which are generally well established, need to be greatly extended and the shifts in the measured frequencies under varying conditions observed and interpreted. Illustrations of a few of the generalizations to emerge from these studies will give an idea of their nature. When a compound, YOH, is dissolved in a solvent X there appears in the infra-red absorption spectrum in addition to the line of normal frequency for OH at 3300 cm^{-1} a second broader line of somewhat smaller frequency which has been interpreted to mean that a part of the YOH molecules form weak compounds with solvent molecules, X, through the establishment of a hydrogen bond. The amount of such association

the same as the time required for the wave-length measurements alone. Several instruments[9] which record the percentages of transmission directly in the near infra-red have recently appeared. They are in fact spectrophotometers. Fig. 5 shows the record made by one of these instruments and was recorded in 35 minutes. It is quite certain that recording spectrographs will generally replace the manual instruments. In addition to saving the worker much time and tedious observation there is a very real advantage from having the original records preserved for future use or comparison.

The problem of molecular structure as it has developed has placed upon the experimental physicist the necessity of continually improving his spectroscopic equipment. While Fig. 2 represents a modern spectrograph for the far infra-red, Fig. 1 is a simple first arrangement. It embodies the essential ideas but has been superseded by instruments featuring many improvements. Ever higher resolution has been required. Fig. 6 represents what higher resolution makes possible in developing the fine structure in the HCl band system. A similar development has occurred in the case of the H_2O molecule at 6μ where in the latest work sharp absorption lines as

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is indicated by the intensity of the displaced OH line.

If several of these compounds Y_1OH, Y_2OH, Y_3OH, etc. are arranged in order of their solubilities, it is found[10] that the shifts of the new lines due to the hydrogen bonds when the Y hydroxides are dissolved in the solvent X are of different magnitudes, the order being the same as that of the solubilities. Reversing this relation it will be evident that where the greatest shifts occur upon association there will be the largest solubilities.

It appears also that the magnitude of the shifts, $\Delta \nu$, which occur when the OH bond is involved in a loose inter- or intramolecular bond can be used as a measure of the energy of such a bond. Badger has proposed the empirical relation:

$$\Delta \nu / \nu \propto D,$$

where D is the energy of the bond.

When the absorption spectra of complex materials of biological importance such as leaves, vegetable and animal tissue, plant pigments, etc. show infra-red absorption lines characteristic of $C-H$, $N-H$, $O-H$, etc. they do not add much to what is known of these materials since chemical studies have already shown the presence of compounds containing these groups. The occurrence of shifts in these lines to lower frequencies might indicate however that some of the complex materials were held together through the formation of hydrogen bonds.

An organic reaction is often accompanied by a minor reaction, a product of which constitutes an impurity in the main product. The presence of such an impurity may be detected and the quantity estimated provided this impurity alone possesses some one of those groups which give rise to an absorption line. While in general such materials can be detected and measured by purely chemical methods the infra method, if applicable, may be very much faster, and in some
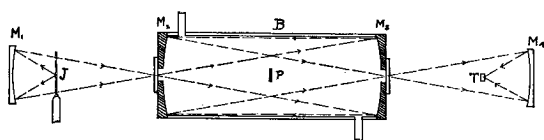

FIG. 8. Apparatus for the measurement of the absorption of gases and vapors in the air by the Pfund method.

kinds of operation this is a very important factor particularly in industrial operations. X-rays have now an established position in many industrial laboratories. The installation of an adequate x-ray equipment would mean that the
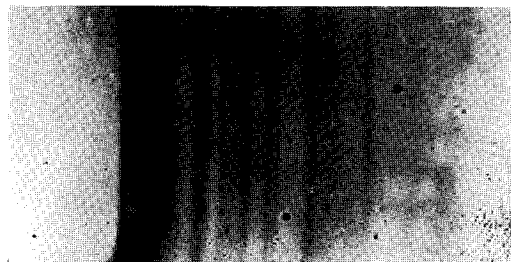

FIG. 9. Evaporograph of furfural ($C_4H_3O \cdot CHO$) between 4μ and 9μ by Czerny method.

x-ray physicist could immediately begin to carry out many well developed tests, and establish lines of research with a certainty of obtaining the results anticipated. It must be admitted that infra-red spectroscopy stands at the threshold only of such a development. It is noticeable, however, that those industries which have established infra-red research laboratories have not discontinued them but rather have amplified them with the passage of time. To date they are found mainly in the oil, gas, and rubber industries.

Infra-red absorption spectra may be obtained without altering, or dissociating the materials under examination, as might occur if ultraviolet light were used. The materials may be in the solid, liquid or vapor phase. X-rays require the materials examined to be crystalline and even then will not locate the hydrogen atoms. The Raman spectra of bonds involved in association seem to be extremely weak and diffuse and require very long exposures while with infra-red the measurements may be nearly instantaneous. Electron diffraction methods require the materials to be in vapor form, which limits their applicability.

In considering the possibilities of infra-red spectroscopy in dealing with complex organic molecules it should not be forgotten that these molecules are not simply aggregates of the groups contained in Table I but are unit structures which have characteristic frequencies. With molecules

of the great complexity of many organic compounds, distortional vibrations may occur of very low frequencies which will lie in the far infra-red. The isomeric forms of such compounds could not be distinguished from each other by the frequencies of Table I since the same groups are present in all the isomers. The shifts in the frequencies of these group lines as the groups took different positions within the molecule would be small and, with a number of isomeric forms present, would be masked. In the far infra-red, however, the frequencies due to distortional vibrations might differ appreciably with the location of the shifting groups. This spectral region appears to offer distinct promise if proper dispersion and resolution are used.

The uses of infra-red spectroscopy most in evidence at this time have already been presented at some length; namely, to obtain data from which the molecular structure of simple molecules may be deduced theoretically, and to study empirically the spectra of the complex organic compounds, tying up as far as possible the chemical properties of a material with its spectrum. There are many other uses some of which may be cited as typical. The absorption of CO_2 gas in long cells at high pressures gave new bands from which it was possible not only to amplify the theory of the structure of this molecule but also to identify bands observed on the planet Venus as due to CO_2, thus finding it possible to add materially to our knowledge of that planet's atmosphere.[11] The results indicate for example that the quantity of CO_2 in this planet's atmosphere is at least one hundred times that found in the earth's atmosphere, while the minimum temperature at the base of the layer is of the magnitude $t > 50°C$.

Applied to other planetary atmospheres certain bands of methane (CH_4) and ammonia (NH_3) have been found on Jupiter, Saturn, Uranus, and Neptune. Employing the sun as source and the atmosphere as absorption cell, the continuous absorption by water vapor has been determined between 8 and 14μ, and the discrete absorptions have been mapped and identified. The problem of the transmission of the atmosphere as a function of atmospheric water vapor is nearing completion. A new atmoshperic layer, comparable to the ozone layer in extent,

and believed to be composed of oxides of nitrogen, has been found. And a graybody temperature of 7000°K has been determined for the sun in the spectral region 8μ to 14μ.

In the field of biology a striking improvement in the method of following the carbon dioxide assimilation and respiration of living plants, which is practically instantaneous, has resulted from developing a spectral absorption method[12] for determining the CO_2 contents of the air. This method is exceptionally sensitive and at the same time remarkably rapid. Through its use in studies of photosynthesis a number of very significant discoveries have been made. The method is equally well adopted to studies of any type of respiration: human, animal, or tissue cultures. It has obviously many uses in quite other fields, including that of industry. Fig. 7 represents the scheme of the apparatus with the absorption cell at the lower left hand. This recording spectrograph is a very excellent example of an infra-red prism spectrometer where the double use of a 60° prism has given the instrument a very good dispersion. Where high resolution is not required such instruments are most advantageously used. Nearly all of the present observations on complex organic molecules are done with prism spectrographs, many of them using the prism but once.

A still more recent[13] method for measuring the amounts of certain gases and vapors found in air, makes use of the infra-red molecular emission and absorption of the gases in question. The method is very sensitive and requires no spectrographic resolution of the infra-red radiation. The scheme of the apparatus employed is shown in Fig. 8, where J represents a jet of the gas to be measured heated to a high temperature, the characteristic radiations from which proceed through the absorption cell B and are focused through a suitable window upon a small receiving chamber T. This chamber, filled with this same gas, absorbs this characteristic radiation with a corresponding rise of temperature which is detected and measured by a couple within the chamber. When air containing this gas is passed through B, the selective radiation is partially cut off from the thermopile receiver with a fall in temperature of the couple which depends upon

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the amount of gas present. No such effect is observed however if this gas is not in the air passed through B. When the gas will not permit heating without decomposition, a solid radiator may be used at J.

A study of the radiation heat from the human body has resulted in the measurement of the emission, reflection, and transmission of infra-red radiation by the human skin. This research[14] in the field of biophysics possesses significance since this information has direct bearing upon the heat-regulating mechanism of the body. Among the results established is that the human skin emits essentially as a blackbody radiator, and that for infra-red radiations negro and white skins reflect about the same.

These illustrations are typical of many that might be presented to show the uses of infra-red spectroscopy in allied fields of science. Carried on as they have been in close collaboration with workers in the other field involved, they represent one of the most promising developments of the present time, where each of the sciences concerned in a problem in a mid-field is capably represented by its specialist. A biologist attempting to solve his problems by the use of highly developed physical equipment or a physicist attempting to enter the biological field, work by comparison under great handicaps. This the industries have long recognized.

Possibly a good way to close a paper which has dwelt perhaps too exclusively with experimental methods, would be to describe a relatively new and very promising method of registering infra-red spectra which, if it succeeds, will render obsolete much of the beautiful infra-red equipment now in use. This method[15] covers one side of a thin film of Celluloid with a suitable absorbing medium; upon the other side a thin layer of a special oil is evaporated. The film and oil together are thin enough to give bright interference colors when suitably illuminated. When a spectrum is projected upon the blackened side, there will be evaporation of the oil from the warmer to the cooler areas. This action is rapid if the film is in a space saturated with the vapor of the oil. The changing thickness of the oil with evaporation will result in a change in the interference colors and the pattern thus produced may be photographed. Fig. 9 shows the infra-red absorption spectrum of furfural in the neighborhood of 5μ. Lines 0.1 mm apart on the photographic plate may be separated. Spectra to 10μ have been recorded.

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