EXPERIMENTAL INFRARED

By John Strong

The infrared spectrum was discovered by Herschel in 1800. He found that a thermometer was heated by invisible radiations when he placed it beyond the red end of a solar spectrum formed by a glass prism. From this primitive discrimination between the visible and invisible, experimental physicists have refined their procedures until now the 15,000 cm^{-1} compass of that invisible spectrum is resolved into some 30,000 separable subdivisions of $\frac{1}{2}$ cm^{-1} width, with prospects of resolving it into 200,000 subdivisions in the near future.

Development of thermal detectors, dispersing means, and auxiliary instrumentation which has made such discrimination possible, constitutes one of the oldest fields of experimental physics. Its century and a half of history is indicated here by the mention of several outstanding instrumental developments which introduce current efforts to improve the obtainable resolving power by a further order of magnitude.

It is noteworthy that many modern detectors are nothing but refined thermometers measuring the temperature rise of a receiver heated by the infrared radiations. A thermopile measures the receiver temperature by the thermoelectric effect; a bolometer measures the temperature of a strip receiver as sensed from its electrical resistance; while Golay's detector is a tiny gas thermometer. For certain restricted regions of the invisible spectrum, other types of detectors have been used—photography has been extended to 1.3 μ, and photoconductive detectors are now available to 5 μ. But, in the main, thermal detectors, which use heating as Herschel did originally, are employed to study this spectrum. It is unfortunate that we do not yet have a detector which has a more direct link between the received electromagnetic energy and the final electrical signal. Since heat is the lowest grade of energy, any detector which changes radiation into thermal energy, as an intermediate form, is intrinsically more inefficient and insensitive than seems necessary. Thermal detectors have been so thoroughly developed that now they are as sensitive as the properties of available materials allow, and their response is recorded with a sensitivity which manifests the unavoidable natural noise (such as Johnson noise and Brownian motion).

John Strong, professor of physics at The Johns Hopkins University, received his PhD in physics at Michigan in 1930 and did research at Caltech and Harvard before joining the Hopkins staff in 1945. During the war he was associated with the OSRD and with the ONR. He is a Fellow of both the Physical and the Optical Societies.

Bolometers, Crystals, and Gratings

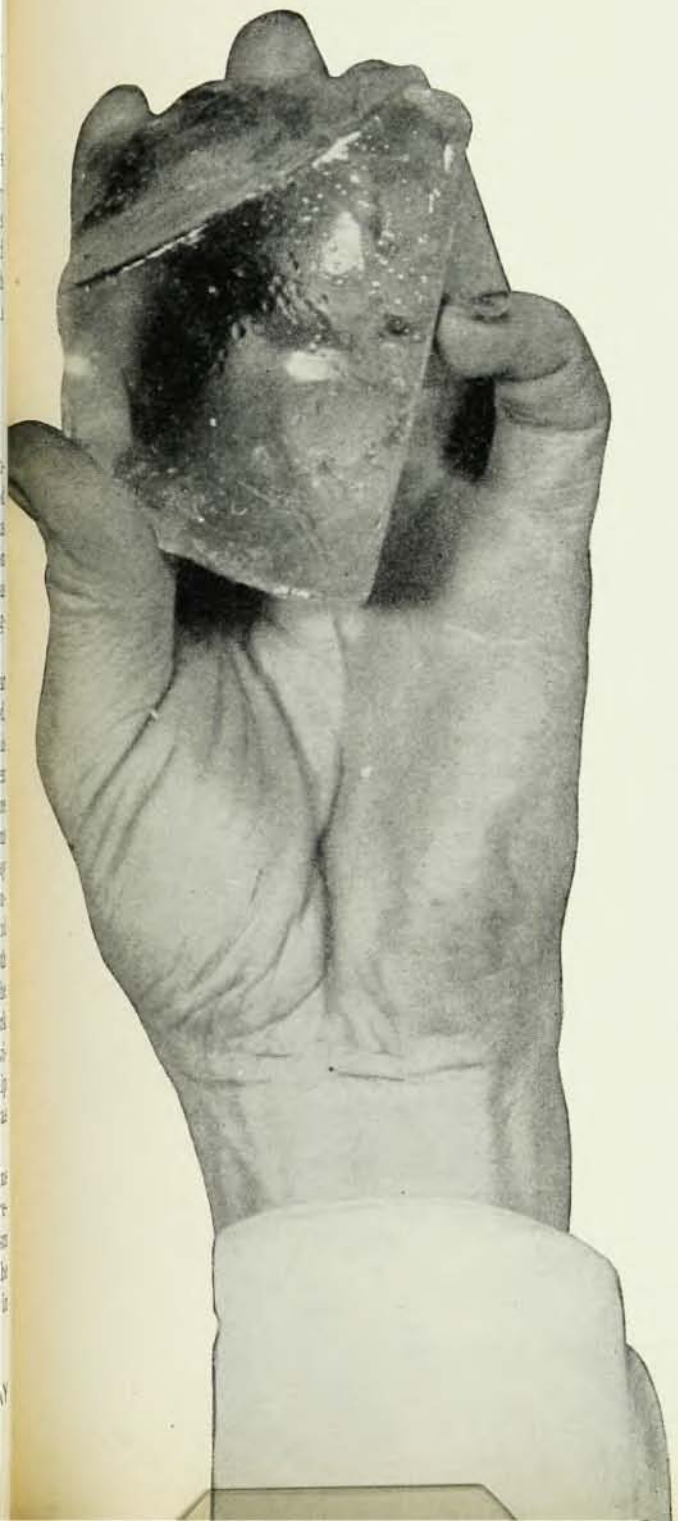
The first great advance in procedure was the invention by S. P. Langley of the bolometer. A second advance was due to John A. Brashear who gave us the methods of working precise optical surfaces on soft materials which are soluble in water, such as rock salt. Two paragraphs from a paper of Langley's (in 1886) describe Brashear's contribution:

"There arose a trouble (common to both solar and lunar spectra in the infrared) of another kind, from the fact that glass is impermeable by this radiation and that rock salt prisms had never been worked of a size or capacity to measure it. We were repeatedly assured by the best European opticians that nothing better could be obtained in this way than the prisms they supplied us, which were incapable of showing a single Fraunhofer line, and we had to search long, both in Europe and North America, first for mines which could furnish the right material, and then for the right man to work it. Having found an artist (Brashear), and previously the material, after a necessary apprenticeship to the use of the latter, this second obstacle was removed."

"Mr. Brashear has worked for us optical trains of this substance of a size, and especially of a precision, heretofore unknown, a single rock salt prism not only dividing the D lines, but showing the nickel line between. We have extensive salt beds in

SPECTROSCOPY

Infrared spectroscopy, a field of physics which has passed through many periods of romantic discovery, has in recent years been of great use to applied research—not only in physics but in many adjacent sciences.



this country, but the material seems to be excavated with so little care and so injudiciously handled that we have been unable to procure specimens at once large and clear. That we now use is from the salt mines of Friederichsthal in Baden. As we have said, however, elsewhere, the chief difficulty lay less in finding the material than the artist."

The introduction of the echelette grating in 1910 by R. W. Wood constituted an advance in technique comparable with the invention of the bolometer by Langley, or comparable with the development of optical surfaces on rock salt by Brashear. This new grating put substantially as much energy in one order of all its spectra as a prism puts in its only spectrum; and, in addition, the grating gave a tenfold greater dispersion than a prism.

H. M. Randall, of the University of Michigan, and his collaborators, W. W. Sleator and E. S. Imes, first used a grating spectrometer in effective combination with a rock salt spectrometer. The latter was added in order to preselect a narrow wave length band and avoid the confusion of the overlapping spectral orders of the grating. The significance of their work was not merely that they achieved far better resolution than had been formerly enjoyed, but that the lines of molecular absorption bands in the infrared were thereafter determinable with the precision necessary to make the study of molecular structure an exact spectroscopic science.

However, the available spectral range was still limited by the opacity of rock salt for wave lengths beyond 15 μ. As a graduate student under Professor Randall's inspiration, it was my privilege to grow the first large alkali halide crystals (of KBr, KCl, and KI, 5″ in diameter and 5″ long) in this country for making the prisms which extended the available spectral range beyond 15 μ almost to 30 μ. Fig. 1 shows a crystal of KBr which I have kept as a souvenir of this work. It is a part of one of my imperfect melts which had double-seeded.

Figure 1. Piece of a large clear single crystal of KBr grown by the author in 1929

There has been a large demand for such crystals and their manufacture has since gone forth under the stewardship of D. C. Stockbarger, working on the crystal growing methods, with H. C. Kremers applying the developed methods on a production scale.

In 1930 one of my own crystals of KBr was fashioned into a prism and Professor Randall and I built a recording spectrometer about it, with which I was able to get methyl halide spectra in the spectral region beyond 15 μ for my doctor's thesis.

Drift was a limitation on the use of this instrument—the detecting system recorded not only deflections due to the desired spectral irradiation but also varying undesired deflections due to variations of ambient temperature, to which the detector was likewise responsive. Drift in the older tedious point-by-point procedure was accounted for by taking an odd number of spaced readings of detector response with "shutter in", together with an even number of interspersed readings with "shutter out". Averages of "in" and "out" readings corresponded to the same time and their difference was free of drift.

Pfund's resonance radiometer, and the other chopped-radiation systems which it inspired, have made modern drift-free recording possible. The modern systems respond to rapid alternating components in the detector signal and ignore the slow changes of detector output which formerly produced drift. Modern systems thus have the effect of continuously taking "shutter in" and "shutter out" readings, in rapid succession, and recording their difference.

Many individuals and groups have worked on improvements of detectors, infrared filters, and new optical materials. The last war gave us PbS, PbSe, and PbTe photoconductive detectors which are sensitive to 3, 4, and 5 μ respectively. R. J. Cashman at Northwestern University, and R. A. Smith's staff at Telecommunications Research Establishment, of Great Malvern, England, are currently improving and developing these detectors, which, within their ranges, are about one hundred times more sensitive than the thermal detectors they replace.

The last war also gave us two important new infrared optical materials, AgCl and KRS5. The latter is a thallium bromide-iodide single crystal material from which lenses or prisms may be fashioned. This material is transparent from the red to nearly 40 μ in the infrared. In addition, at the Bureau of Standards, E. K. Plyler has recently demonstrated the usefulness of caesium bromide in single crystal form as an optical material for this region. Crystalline quartz becomes opaque at about 3 μ; but, in thin plates, it is again transparent enough for use as a window material for thermal detectors by $\lambda = 40\,\mu$. By $\lambda = 80\,\mu$, and beyond, quartz is transparent enough to be used for lenses. Mainly due to these properties of quartz, research has been easier in the past beyond 40 μ than it has been in the region 20–40 μ, where little work has been done for the want of a transparent material. With the new optical materials this gap in the observable region is removed.

Today, as a result of all these developments, one can procure, from any one of several firms, almost foolproof instruments provided with alkali halide prisms and drift-free detectors. These instruments, with pen recorders, will automatically write the transmission of a gas, liquid or solid sample directly as an ink line on paper.

Prospects for Infrared Instrumentation

A significant part of an experimental physicist's energies are properly concerned with the choice, from among the many problems whose solutions would make a significant contribution to science, of those which he himself can solve with the facilities at hand, or, if they are improvable, with facilities he can develop.

When I came to Hopkins in 1946, with the opportunity to work again in the experimental infrared field, I decided to attempt an improvement of spectral resolving power—especially since this was necessary to carry out the plans I had in mind. This quantitative examination of instrumental limitations now promises, in its fruitfulness, to be an experience quite parallel to our recent examination of the limitations of diffraction grating ruling engines.

Fig. 2 shows a diagram of the infrared spectrometer which is to be improved. One wants a spectrometer to yield high resolving power coupled with a high ratio of signal-to-noise in detector response. If the resolving limit $\Delta\nu$ is not as small as desired, then the spectroscopist will narrow the entrance and exit slits. This can be done effectively as long as

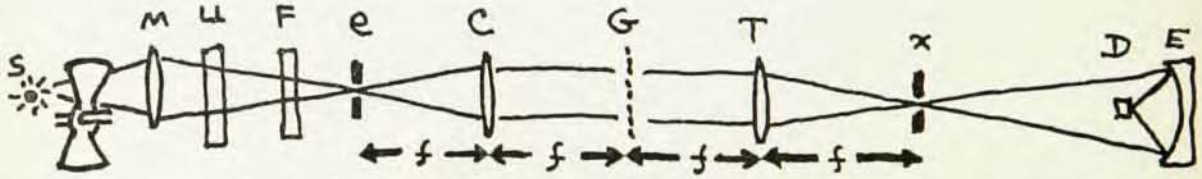


Figure 2. High Resolving Power Spectrometer. S is black body source focused on entrance slit e by lens of mirror M through the unknown U and a filter F (to remove higher order spectra of the grating G). C is the collimator of focal length f and T is the telescope which focuses the spectrum across the exit slit x. Monochromatic radiations are focused by the elliptical mirror E on the detector D.

diffraction does not limit the improvement of resolving power, or as long as energy deficiency does not limit it.

The diffraction limited resolving power, in the first instance, is

$$\Delta\nu_d = \frac{1}{b \sin\theta}$$

Here b is the width of the grating and θ is the direction of the incident and diffracted beams.

The energy-limited resolving power in the far infrared, in the second instance, is

$$\Delta\nu_e \sim \sqrt{\frac{f}{AT_s \frac{d\theta}{d\lambda} l}}$$

Here A is the cross sectional area of the transmitted parallel beam; T_s is the temperature of the source; $d\theta/d\lambda$ is the dispersion; and l is the slit length.

Actually, the laboratory resolution limits currently attained with thermal detectors are $\Delta\nu = \frac{1}{2}$ cm^{-1}. Here the resolution is energy-limited rather than diffraction-limited, since, for the gratings involved ($b \sin\theta = 10$ cm), $\Delta\nu_d = \frac{1}{10}$ cm^{-1}.

From the expression for $\Delta\nu_e$ it is seen that the resolution limit is smallest, meaning greatest resolving power, when the dispersion of the prism or grating is greatest. Accordingly, since prisms are some ten times inferior to gratings in dispersion in the infrared, we have been led to devote some little attention to improvements in ruling engines in order eventually to have larger gratings. For example, 15-inch gratings, when available, will yield an improvement of fourfold in A, the area of the dispersing element, over currently used gratings. From the expression for $\Delta\nu_e$ this will give an improvement in resolving power of $\sqrt{4}$. These 15-inch gratings may still lie far in the future but current success with a new 14,400 lines per inch ruling engine, for 6-inch gratings, convinces us that the necessary larger engines to rule them are possible. (The new 6-inch gratings exhibit $\frac{1}{10}$ per cent ghost intensity in the first order and substantially theoretical resolving power.) In the meantime, before a large engine is available, it will be possible for us to use a mosaic of four presently available gratings (phased to give full resolving power).

The useful length of slit is limited by increased off-axis aberrations, and by increased light losses from shadowing, or so-called vignetting, as the ends of the longer slit remove farther from the optical axis. We have made studies of aberration and have devised means to restrict losses of radiation by vignetting. As a result, it will be possible to increase l, the length of the slit, threefold over currently used slit lengths. We plan to use an elliptical mirror giving a sixteenfold reduction in the image of the exit slit on the detector, as compared with the customary fivefold reduction. We can thus keep the detector area unchanged; as well as the focal lengths of C and T and the over-all efficiency of the optical system. This increase of l should give a gain of threefold in energy, or $\sqrt{3}$ in resolving power.

A further gain will come from increasing the source "brightness". We have found that a carbon arc is an excellent infrared source since the very high temperature positive crater is self-regulating. We have also recently developed a high temperature tungsten source for infrared spectroscopy. In the laboratory either of these higher temperature sources will surpass the customary globar source in spectral brightness by a factor of at least 4, to give a gain of $\sqrt{4}$ in resolving power.

We are now constructing an infrared spectrometer at Hopkins which combines these improvements. We expect all these, and other improvements, to yield a resolution limit for laboratory studies which will be seven times better than current grating spectrometers. The resolving power for a solar spectrum should be two to four times better. This expected limit of $\frac{1}{14}$ cm^{-1} for laboratory studies is imposed both by flux and detector sensitivity limitations and by diffraction effects. Since spectral line breadths are also about $\frac{1}{14}$ cm^{-1}, these coinciding limitations make a comfortable combination all around.

Our Hopkins program is not alone in its promise of achieving better resolving power than has been enjoyed heretofore. For example, Marcel Golay has devised two ingenious multiple slit systems; both of these make it possible to use a set of several entrance slits on a spectrometer in parallel juxtaposition. In the first of Golay's systems the radiation through each entrance, and through each exit slit, is suitably chopped or modulated, and the signal obtained from a single detector, which receives the radiation from all the exit slits, will be a measure of the energy in the narrow spectral band defined by the width of a single slit. In the second system a multiplicity of fixed and unmodulated slits are used—the difference between two large bundles of radiation from the exit slits constitutes a measure of the energy in the narrow, one slit wide, spectral band. Either of these systems permits the utilization of narrower slits for the sake of increased resolution. Conversely, in instances where the resolution limit is determined by diffraction of a prism

or grating, Golay's system can be used either to improve the ratio of signal-to-noise or to improve the speed of a system, without sacrificing resolution. The second multiple slit system is being used by Shirleigh Silverman at the Johns Hopkins Applied Physics Laboratory to improve speed and thus make possible his studies of the spectra of explosive reactions as they depend on time. The spectra Golay gets are displayed on a cathode ray tube screen in 50–100 milliseconds. Fig. 3 shows Golay's spectrum of some lines in the NH_3 band at 10.5 μ, as reported at last October's meeting of the Optical Society. This spectrum exhibits the same resolving power which we were able to get, a decade or so ago, only after tedious point-by-point string pulling and plotting.

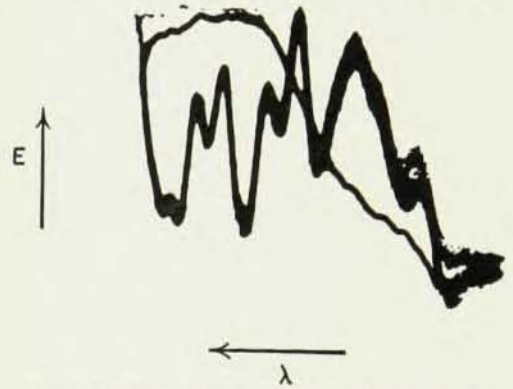


Figure 3. Golay's 80-slit spectrum of ammonia at 10.5 μ with a NaCl prism with f = 38 cm and equivalent single slit width 0.1 mm. Golay's system displays this spectrum seven times per second.

Infrared in Physics

In the past century, the measurements of black body radiation, using primitive thermal detectors, revealed the experimental enigma which required the invention of the quantum theory for its explanation by Planck.

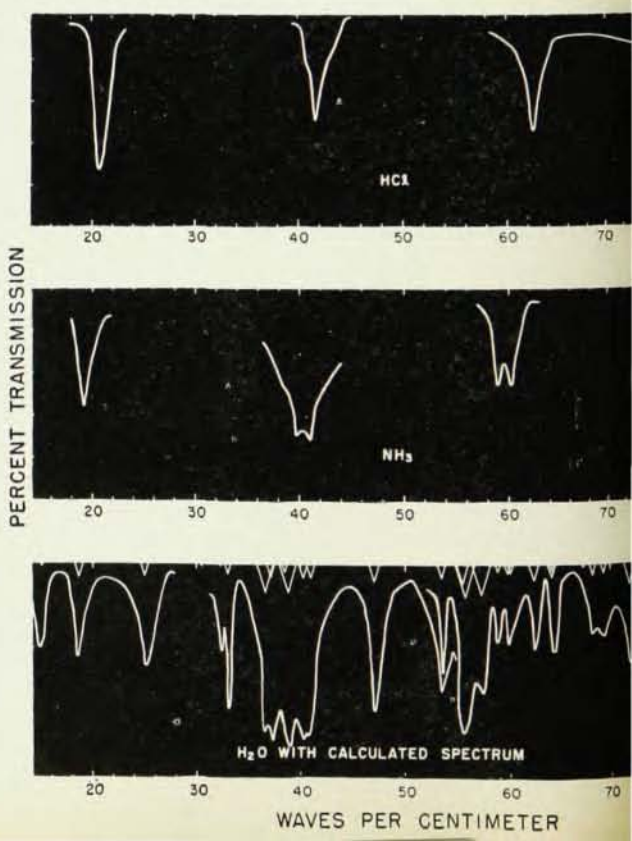
In modern physics the experimentally measured energy changes of molecules, falling in the infrared spectrum, have provided the quantum mechanicians with an extensive and precise experience for testing the elaborate deductions from the mystical propositions of quantum mechanics. Molecular absorption lines are due to quantum changes of molecular energy which, in turn, depend on the structure of the molecule. The infrared spectrum may be divided into categories according to the different origins of molecular absorption lines, as follows:

Absorption lines in the microwave region are largely due to transitions between the lowest energy states of molecular rotation. The more intense of the molecular rotation lines, originating from transitions of high probability between highly populated energy states, lie mostly in the spectral region beyond 20 μ wave length. Bands of lines, lying between 2 and 20 μ, are due to transitions involving simultaneous quantum changes of vibrational and rotational energy (although some bands, arising from bending vibrations of very large molecules, lie in this so-called pure rotation region, $\lambda > 20$). Below 2 μ, the absorption bands are associated with harmonic and combination vibration frequencies, or with transitions involving vibrational and rotational energy and a simultaneous change of the electronic energy of the molecule.

The pure rotation lines of molecules having a permanent electric dipole moment have a special interest for the experimental physicist on the one hand because of challenging experimental difficulties and on the other because of the relative simplicity and interpretability of observations.

The three gases which have been studied most in the far infrared are NH_3, HCl, and H_2O. McCubbin and Sinton have extended all these studies to longer wave lengths and some of McCubbin's latest spectra are shown in Fig. 4.

Figure 4. McCubbin's spectra in the extreme infrared. Notice the water absorption line at 666 μ; and also, the absence of doubling in the first ammonia line.



Infrared in Chemistry

Detailed quantum interpretations exist only for the simpler molecules. However, both academic and industrial chemists have discovered that the infrared spectrum of a molecule is a highly differentiated molecular property (even in the solid and liquid state where it is less unique than in the vapor state). This empirical use of the infrared spectrum as a molecular property has been widely applied over the last 15 years. In the vapor phase a molecule can "call out" an absorption line, or not, for each one of the present 30,000 subdivisions of the infrared spectrum. This empirical use of the infrared is the flowering of the pioneering work of W. W. Coblentz, of the Bureau of Standards, done nearly a half-century ago. Such empirical methods have recently guided chemists in the synthesis of penicillin and in the identification of certain biological steroids, both chemical works of great importance. In the future, when the infrared is resolved into 200,000 subdivisions, complex molecules in the vapor phase will exhibit spectra which are far more characteristic than they are with the resolving powers presently employed. When applied to the study of compounds which have a vapor pressure of only a few microns (such as have been heretofore studied only in the liquid phase), it is to be expected that the empirical methods which have proven so useful to chemists in the past will then prove even more powerful in determining the associations of radical groups and the general features of molecular structures.

Infrared in Geophysics

In addition to its importance in pure physics, and in chemistry, as I have intimated above, the infrared has applications in astrophysics and geophysics. The aggregate of radiations emitted over the surface of a planet is expected to represent an energy transfer which balances the energy reception by solar radiation. By virtue of the low temperatures of planets, their emitted radiations lie in the infrared spectrum. The infrared spectra of the molecules of planetary atmospheres are of primary concern to astrophysicists and geophysicists because of their bearing on planetary atmospheric transmission; and because of their importance in the mechanism by which energy is transferred in and through layers of such atmospheres by radiation; and finally, their bearing on the nature of the radiations emitted by a planet, or our earth, into the cosmic cold.

The transmission of our own atmosphere in the infrared for solar radiations has an interesting history and a provocative future. Fig. 5 shows part of S. P. Langley's 1887 measurements for atmospheric transmission in the region 7–14 μ. During the last war I noticed that no recent writer had appreciated this part of his results. This was not odd because the 1887 indices of refraction for NaCl which Langley used gave fallacious wave lengths. I found that his observations become significant, however, when

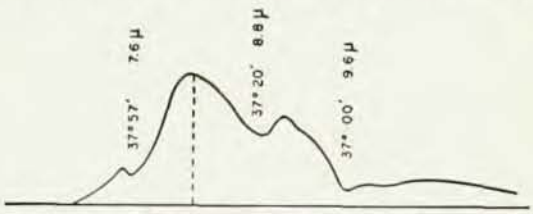
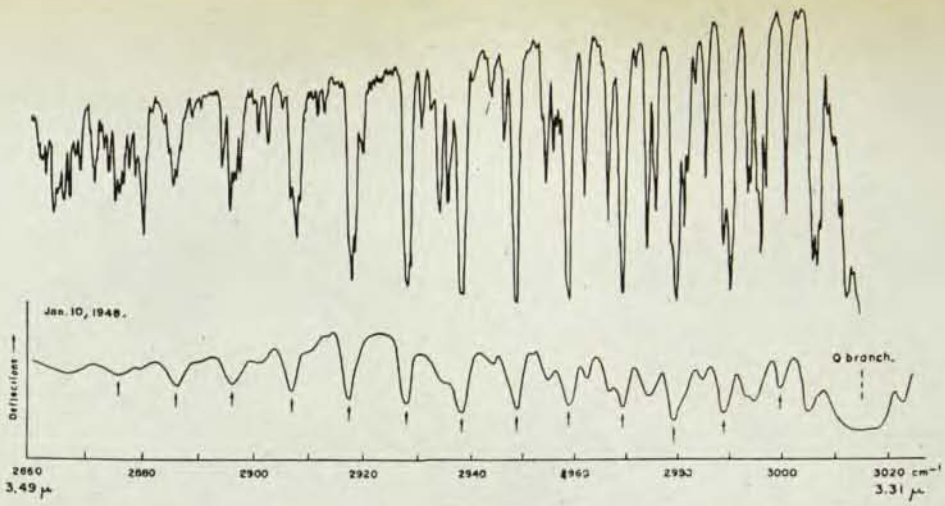


Figure 5. S. P. Langley's solar energy curve showing atmospheric absorption bands. Taken in 1887.

his fallacious wave lengths were replaced by the correct ones derived from his published deviation angles. Fig. 5 shows the absorption bands which Langley discovered at 7.6 μ, 8.8 μ, and at 9.6 μ. Langley said that the 7.6 μ band (now known to have been due to N_2O) was best observed in winter while the 8.8 μ band (which I suspect was due to SO_2) was best observed in summer. The 9.6 μ band was the π-band of atmospheric ozone.

While on the subject of the atmospheric bands caused by minor atmospheric constituents, it is cogent to relate the recent exciting discovery of M. Migeotte that there is a substantial amount of methane in our atmosphere. Although we are accustomed to the idea of methane in a planetary atmosphere, its discovery in our own atmosphere came as a surprise to most of us. Migeotte's methane lines are marked on the lower spectrum of Fig. 6 by arrows. A subsequent spectrum which W. M. Benesch has obtained here at Hopkins, with a substantially better resolving power, is shown above in Fig. 6. Migeotte is continuing his work at an enviable high altitude observing station in Switzerland on the Jungfrau at 3456 meters, with a resolving power now equal or superior to any. We are also continuing our study of this atmospheric constituent. Such a study may reveal its origin, which may be from the marshy places on the earth; or it may come from similar but prehistoric decompositions only recently vented into the atmosphere from oil and gas fields; or, finally, it may be generated in the upper air.

Fig. 7 shows our use of a war surplus 60-inch army searchlight, as a source, to measure the absorption of infrared radiation by surface air under high resolution. Over an 800-foot surface air path both CH_4 and HDO, but not N_2O, were detected.



If this equipment were more portable it might be used to prospect for natural gas deposits.

In our studies of atmospheric transmission it has been our good fortune to have at our disposal a double KBr monochromator. This instrument was constructed before the war for use on the 200-inch telescope to observe the spectra of the sun, moon, and planets. Recently, we were fortunate to have this monochromator taken aloft by the Air Force in a B-29 aeroplane to altitudes of about 11 km. At these altitudes sun-seeking mirrors (provided by Roger Estey's group at the Naval Ordnance Test Station, Inyokern) supplied the monochromator with solar radiations to be analyzed. Fig. 8 shows the atmospheric transparency over the wave length range from 8 to 25 μ which was observed at those altitudes. An accompanying black body spectral energy distribution for stratospheric temperatures is plotted in dots. This dotted line indicates the importance of the various spectral regions for discharging the heat which the stratosphere receives by ultraviolet solar radiation.

Coupled with these B-29 observations, a hypothesis of my own, happily fortified by some analysis by my colleague, G. N. Plass, has provided for the first time a basis of explanation of the isothermal character of our stratosphere. It also explains the sudden vanishing of the derivative of temperature in the troposphere (the lapse rate) at its inferior boundary. By virtue of the pressure broadening of spectra lines, Dr. Plass and I infer that lower layers in the stratosphere are expected, paradoxically, to discharge heat to the cosmic cold by radiation at a greater rate than superior layers. We envision that the disappearance of the lapse rate at the tropopause occurs where upward convection of heat is first dominated by this apparently unnatural heat transfer situation.

A large absorption cell has been set up at Johns Hopkins for measuring the effect of pressure on the infrared absorption of atmospheric gases. This cell can be either evacuated or pressurized and it provides absorbing paths of 300 feet, 600 feet, and higher multiples. Observations have already been collected on the effect of nitrogen pressure on absorption by water vapor in the spectrum from 12 to 22 μ. These results, and others forthcoming for CO_2 and O_3, will be particularly useful for detailed calculations of heat transfer in the stratosphere, and troposphere; although they have some purely physical interest as well.

With further refinements, we hope that our studies of pressure broadening in the big tube will eventually provide a method for revealing intermolecular forces in the vapor phase. If specific intermolecular forces between certain unlike molecules should exist, such as some biophysicists have suspected, there should be some corresponding manifestation in the simpler molecules. We plan to look for such manifest effects as we pressurize an absorbing gas with various non-absorbing molecules.

The infrared is a field of physics which has passed through several periods of romantic discovery and it has established its utility in applied science. In this article I have emphasized those aspects of the wide and active field of infrared spectroscopy which appeal particularly to us here at Hopkins. This is not the place to mention many other phases of infrared research. Those interested in supplementary reading will find a large bibliography in the paper of Van Zandt Williams, "Infrared Instrumentation and Techniques", in the *Review of Scientific Instruments*, March 1948. I have attempted to supplement rather than duplicate this fine review.

The support of our work since 1945, by the Office of Naval Research, is acknowledged.

Figure 6. Lower spectrum—Migeotte's 13 lines of CH_4 in the solar spectrum. Above —Benesch's spectrum under higher resolving power. The line marked X is also due to methane.

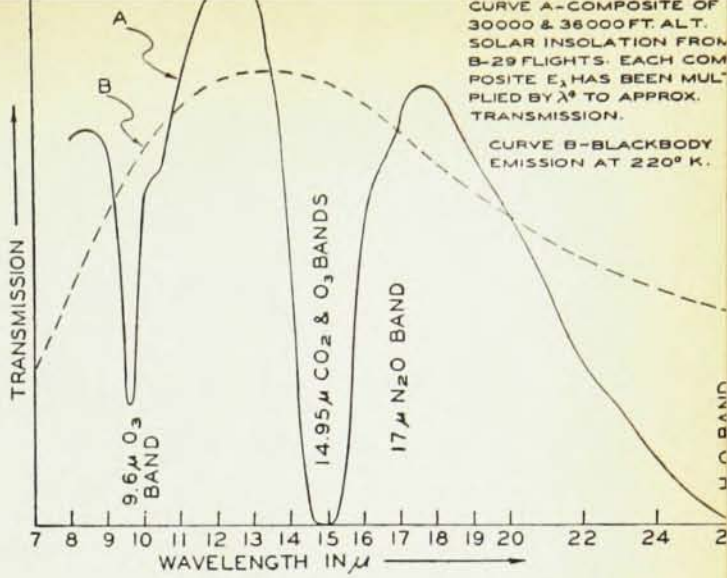


Figure 8. Transmission of the atmosphere above 11 KM

Figure 7. War surplus 60-inch searchlight (with window removed) in improvised wind shelter and projecting onto apparatus in top floor laboratory. This gear was used to measure atmospheric transmission. HDO and CH_4 lines were detected.