

POSSIBILITIES OF ASTRONOMICAL SPECTROSCOPY IN THE INFRARED

P. SWINGS

Investigation of the infrared region of astronomical spectra is a most promising avenue of pure research. Considerable experimental progress is now being made in the study of the infrared, most of it cloaked in war secrecy. Theoretical considerations, however, make it clear that, despite the barriers due to atmospheric absorption, there are enough spectral windows to furnish results just as interesting as the ultraviolet region has furnished in recent years.

The infrared region is commonly divided by astronomers into "photographic infrared" extending from the visual red to $1.35\ \mu$ and "thermoelectric infrared" extending from $1.35\ \mu$ to $24\ \mu$, the limits corresponding, respectively, to the photographic and thermoelectric methods of recording. Several other techniques which are now available will be discussed in this paper.

THE PHOTOGRAPHIC INFRARED

Astronomical spectroscopists are now devoting well-deserved attention to the photographic infrared. Pioneering work at the Lowell and Mount Wilson Observatories has led the way by investigations of the sun, planets, and stars. Some results have been obtained on the infrared spectra of the solar corona, the aurora, and the night sky. Nothing is known, however, about the infrared spectra of comets and very little about that of nebulae and peculiar stars.

In speaking of the extension of a spectral region one should keep in mind that as far as the atomic lines are concerned, only the energy scale, hence the wave-number scale, is of importance, not the wave-length scale.¹ The spectral region in the infrared from $\lambda\ 7000$ to $\lambda\ 10,000$ is, roughly speaking, as important as that in the ultraviolet from $\lambda\ 4000$ to $\lambda\ 3400$, since each of these regions covers approximately $4300\ \text{cm}^{-1}$. It is well known

¹ Stars like α Cygni have fewer absorption lines per angstrom in the red than in the ultraviolet. This is not true of the number of lines per wave-number unit.

that the study of astronomical spectra in the ultraviolet has been most fruitful, and an extension of as many wave-numbers toward the infrared should be equally productive. Ranges in angstrom units do not have the same significance, however, an extension of 10,000 angstroms from λ 7000 to λ 17,000 being equivalent to an extension of only 1000 angstroms from λ 4000 to λ 3000. One spectral region may be more favorable than another for the detection or investigation of specific atoms; this is especially significant for molecules. For example, the near infrared may reveal molecules through their vibrational bands which could not occur in the visual or ultraviolet region.

Only a few of the data probably to be obtained by observation in the photographic infrared are listed here.

a) Many forbidden lines, especially those due to metals, should appear in peculiar bright-line stars, novae, and possibly nebulae; those which correspond to low excitation may reach considerable intensity.

b) Lines of various light elements, such as O I and N I, are strong in the infrared and should provide valuable information especially in stars with extended atmospheres. Certain infrared lines of C II, C III, and other elements, would permit a more thorough discussion of the selectivities present in O stars, P Cygni, and Be stars. Interesting results will also be obtained from the Me stars.

c) New molecules, mainly polyatomic, should be found in comets, and possibly also in planets and satellites.

d) New diatomic molecules may be found in late-type stars and possibly even triatomic molecules.

In fact an extension of the covered spectral range is always necessarily fruitful, and there is no field of astronomy that would not profit by it. The extension of astronomical spectroscopy toward the photographic infrared depends for its success on having the proper instruments; for example, high quality echelette gratings ruled for that region are essential.

THE THERMOELECTRIC INFRARED

The region of astronomical spectra most commonly photographed extends from λ 3100 to λ 7000, a region $18,000\text{ cm}^{-1}$

wide. Solar radiation has been measured thermoelectrically, with thermopiles, bolometers, and radiometers from 1 to 24 μ , an extension of more than 10,000 cm^{-1} . Even if only a small part of the infrared is observable in a specific object, on account of atmospheric absorption or because of technical difficulties, it would provide a valuable addition in observational material.

Thus far high resolution in the thermoelectric infrared has been applied only to the sun,² stellar investigations having been made only with very low resolving power. In view of the recent progress in receivers and amplifiers there is every reason to believe that practical instruments could be designed also for high dispersion spectroscopy of stars and planets, especially for work at the coudé focus of large reflectors. Great improvements are being made in receivers and recorders, such as thermocouples made from evaporated films; sensitive bolometers employing special amplifiers; very fast photographic recorders; and the application of oscillographic methods. All these data will become available to astronomers when war secrecy is no longer desirable. Doubtless there will always be practical difficulties in thermoelectric recording instruments, such as those due to unavoidable variations in the illumination of the slit, and the limitations in sensitivity of thermal receivers due to thermodynamic fluctuations.

Whatever the thermal receiver may be,³ it cannot accumulate the effect of radiation like a photographic plate. Hence the desire to find methods of infrared photography, especially methods in which accumulated effects can be utilized. Moreover, the conversion of quanta of radiation into heat in a thermal receiver is very inefficient compared to the action of light-quanta on a photographic emulsion.

² Even for the sun the important work of Adel, Lampland, Migeotte, and others was only pioneering.

³ Sir William Herschel discovered infrared radiation in 1800 by placing the bulb of a thermometer in dispersed sunlight and observing that heating of the thermometer still took place beyond the red end of the visual spectrum. Actually the effect increased to a maximum well beyond the limit of the visible red. Herschel's thermometer was the ancestor of all thermal receivers.

METHODS FOR PHOTOGRAPHING INFRARED

Of the five known methods of infrared photography,⁴ two may be considered as direct, three as indirect. Photographic emulsions especially prepared and sensitized to the infrared by means of dyes (first direct method) may be used, or one may apply the fact that an exposure to infrared is able to destroy the latent effect of a previous exposure to radiation of shorter wave length (second direct method). Photography may be based on the volatilization of a thin layer of material when exposed to infrared (evaporography, first indirect method); or on the extinction by exposure to infrared of the glow of a phosphorescent screen previously excited by shorter wave lengths (phosphorography, second indirect method). Finally, electronic methods may be employed, making use of electron-image tubes (third indirect method). In the indirect methods, the surface on which the record is made is later photographed on an ordinary emulsion.

Infrared photography with emulsions sensitized by dyes.— It is well known that, by using sensitizing dye solutions, photographic emulsions can now be prepared which are sensitive to the near infrared region. The discovery that an emulsion may be color-sensitized by means of a dye was made by the German astronomer, H. W. Vogel, in 1873. The sensitizing dye solutions have been the subject of a considerable number of investigations, especially in the laboratories of the Eastman Kodak, Ilford, and Agfa Companies.

The dyes used in the early days were mostly eosin and erythrosin, while recent progress has been mainly based on the derivatives of quinoline. Xenocyanine extended the photographic limit to 11,000 Å, and the pentacarbocyanines to beyond 12,000 Å.

Up to λ 8900 photographic plates are quite sensitive, but the sensitivity reached between λ 9000 and λ 12,000 is very low. Beyond λ 12,000 the use of plates is possible only for extremely bright sources such as the sun or intense laboratory sources. In

⁴ Walter Clark, *Photography by Infrared* (New York, 1939), chapter vi.

stellar spectrography it is indeed difficult at present to work beyond λ 8900; in the region λ 8950– λ 9800, closely packed telluric lines would render the observations very difficult anyway. The hypersensitization of the red or infrared sensitive plates with ammonia is well known.

Infrared photography by means of the Herschel effect.—In 1840 Sir John Herschel, son of Sir William, discovered the property of the red rays of the spectrum to reverse, or at least to reduce, a visible printing-out image on silver chloride paper. Immediately after Herschel's publication, the phenomenon which received the name of Herschel effect was subjected to much study, particularly by Becquerel in France. After the discovery of the latent image, an account of which was published by Henry Fox Talbot in 1841, it was found that the latent image produced by exposure to light of shorter wave length could also be destroyed by exposure to light of longer wave length. A. P. H. Trivelli (1929) has called this the latent Herschel effect, to distinguish it from the original visible effect. The Herschel effect has recently been the object of considerable investigation in the University of Liège, Belgium (1941 to 1943), and in the Kodak Research Laboratories (1943).

In fact so many conflicting experimental results have been reported that it would seem that the effect is not general, but depends on the photographic material used and on the experimental conditions. Before infrared sensitized plates were developed, the latent Herschel effect was used to photograph spectra in the infrared; for example, A. Terenin, in 1924, used it to record spectra up to 11,300 Å. Actually the investigations of the Herschel effect stimulated the study of the sensitizing and desensitizing dyes with the well-known successful results.

From numerous experiments it appears that up to 10,140 Å the sensitivity of the photographic method based on the Herschel effect is about the same as that obtained with the new sensitized emulsions. The study of the Herschel effect is of considerable importance for the understanding of the elementary photographic processes. Moreover the method is still useful in the production of direct positives in cameras, in the making of composite pictures, in printing negatives of high contrast, and in duplication

of cinematograph negative films; but its astronomical applications appear to be very limited.

The evaporographic method.—If the infrared spectrum is received on a thin layer of a substance which sublimates or vaporizes easily, part of the material is sublimed or vaporized away from the regions exposed to infrared radiation and deposited on the cooler, unexposed regions. If the changes in thickness of the layer can be observed, they will reveal the intensity distribution in the infrared spectrum.

The layer should be in an enclosed volume which would thus be filled with saturated vapor of the substance used. When the exposure to radiation is interrupted, the irradiated regions return to room temperature and the changes in thickness should, in ideal conditions, stop, since the substance is then in equilibrium with its vapor, and the number of molecules released by evaporation or sublimation at any point equals the number of molecules deposited at that point.

It is hoped that a detailed discussion of the evaporographic method will be ready for publication in the next issue of this magazine.

The phosphorographic method.—The fact that phosphorescent light is rapidly extinguished if exposed to infrared radiation has been known for 140 years, and its possible application to infrared spectroscopy was recognized by Draper as early as 1885. It deserves further study since it would probably lead to interesting astronomical applications. Actually when a phosphorescent light is exposed to infrared there is first an increase in the brightness of the glow, followed by a rapid decrease. In other words the total amount of accumulated energy is emitted more rapidly. Different infrared wave lengths also affect the phosphorescence more or less rapidly. But the final effect is that the phosphorescence in the parts exposed to the infrared is always substantially diminished before the general background glow has decreased much.

* Materials commonly used are calcium sulphide, zinc sulphide, zinc silicate,⁵ and copper-activated zinc cadmium sulphide. Many

⁵ The common names of these three materials are Balmain's Paint, Sidot blende, and Willemite.

suggestions have been made for phosphorescent screens having a long afterglow, rapidly extinguished by exposure to long wavelength radiation. Addition to the phosphorescent screen of traces of salts of iron or nickel which have strong infrared absorption accelerates the extinction. Progress seems to have been made recently in improving the graininess of the screen, an important improvement since graininess limits the resolution.

The phosphorescent material may either be spread in a thin layer on a glass plate or pressed into a plastic material. It must be excited by proper radiation, the most convenient source being the quartz mercury arc (exposure of the order of a minute). The luminous screen is then exposed for a given time to the infrared spectrum, after which it is placed in contact with a photographic plate sensitive to the phosphorescent light so that a permanent record is obtained.⁶ If the plates are sensitive only to the blue, the material must have a blue phosphorescence like that of calcium sulphide, which, however, has a rather coarse grain and gives off hydrogen sulphide which may affect the photographic plate. The use of orthochromatic and panchromatic plates extends the field of suitable phosphorescent materials. The infrared sensitivity of a phosphorescent screen is not uniform for all wave lengths. For example, zinc sulphide has a minimum of sensitivity near λ 11,000. The infrared limit of extinction differs also for different materials.

The reciprocity law holds for the extinguishing action of infrared radiation, the effect depending only on the product of the intensity of the infrared radiation by the time of exposure to it. Moreover the "characteristic curve" of a phosphorescent layer is very similar to that of a photographic plate. Hence the phosphorographic method should give spectrograms of excellent quality, at least if the grain of the material is small and if the plate and screen are in very good contact.

No attempt will be made to discuss here the numerous problems related to the phosphorographic method. The infrared limit has been claimed to be somewhere around 18,000 Å, de-

⁶ Evidently a direct recording may also be obtained by some kind of photoelectric device. Where a photographic record is not taken by contact the method is called phosphorographic.

pending on the material and technique. In 1906 H. Lehmann designed an "infrared phosphorescent spectrograph" which was used by A. Bergmann (1908) to obtain emission lines of the alkali metals to 17,000 Å.

Except for the examination of the solar spectrum to 10,000 Å about fifty-five years ago, there does not seem to have been any astronomical application of the method. Important progress is being made at present in the field of phosphorescence, especially in relation to war problems, television, and electron microscopy. The postwar astronomical applications will probably be of great interest.

Infrared spectrography employing the electron-image tube.— Suppose that we project an infrared spectrum on an infrared sensitive photoelectric surface. Electrons will be emitted from the surface in proportion to the amount of incident radiation. Close to the cathode the electrons will thus form an electrical reproduction of the spectrum. These electrons can then be accelerated and brought to a focus by electrostatic means. In the focal surface a fluorescent screen will then give a visible image of the spectrum which may be photographed if a permanent record is desired. A simple "electron lens" produces inverted images with curved field and pin-cushion distortion; but the aberrations can be corrected satisfactorily by electrical means.

With the present photoelectric surfaces, the method is not effective beyond $1.7\ \mu$. But, as in the methods previously discussed, considerable progress is being made in the fields of television, electron microscopy, and electron telescopes; hence interesting postwar astronomical applications are probable.

THEORETICAL INFRARED LIMIT OF THESE METHODS

Is there any hope that photographic plates sensitized with adequate, still-unknown dyes may some day be used in the infrared well beyond the present limit ($1.35\ \mu$), perhaps beyond $2\ \mu$? This question can be answered in the negative for two reasons. The first, mentioned by Czerny, and considered in detail by G. Kornfeld⁷ (1938), involves the reaction which the molecules of

⁷ *Jour. Chem. Phys.*, 6, 201, 1938.

the sensitizing dyes would undergo as a result of absorbing infrared radiation emitted by the surroundings. Kornfeld's investigations show that infrared sensitizing beyond 20,000 Å would be impractical.

The second reason which has been discussed by Czerny is very fundamental and involves the "dark space radiation." It applies to all three methods of infrared photography and to the electron-image tube but not to evaporography.

We know that the infrared sensitized plates commercially available must be preserved in a refrigerator to avoid fogging. We will now show, following Czerny,⁸ that if photographic emulsions were sensitive to longer wave length (beyond 2 μ) they would have to be kept all the time at extremely low temperature, an impossible condition at all stages of the preparation, handling, and use of the plates.

At room temperature the black-body radiation which is present everywhere does not contain an appreciable number of quanta of radiation of the visual or near infrared region. Similarly there is practically no air molecule having a kinetic energy equal to that of a quantum of visual radiation. But the situation is entirely different at longer wave lengths. For example, a considerable number of quanta of wave length 4 μ are present in the black-body radiation at room temperature, and at that temperature a considerable number of molecules have a kinetic energy equal to a quantum at 4 μ . Hence for a plate sensitive to 4 μ the photographic process would proceed quite fast in the dark at room temperature.

Table I, taken from Czerny's paper, furnishes illuminating data on this subject. Column 2 gives the number of quanta for the various spectral ranges (column 1) at $T = 290^\circ \text{ K}$ (17° C), computed from the Planck formula (which in this spectral region is approximated well enough by Wien's law). The figures of column 2 show how abruptly the numbers of quanta increase in the infrared at that temperature. Column 3 gives the distances at which a Nernst burner should be placed to give the same num-

⁸ *Zs. f. Phys.*, **53**, 1, 1929.

ber of quanta, the filament having a total area of 0.1 cm^2 at 2300° K .

TABLE I
CHARACTERISTICS OF BLACK-BODY RADIATION AND MOLECULAR
ENERGIES AT ROOM TEMPERATURE

λ	Number of Quanta Received per Second on One Side of an Area of 1 cm^2 at $T = 290^\circ \text{ K}$	Distance in Meters of a Nernst-filament Furnishing the Same Number of Quanta	Number of Air Molecules of Kinetic Energy Equal to $h\nu$, Encountering an Area of 1 cm^2 per Second
$< 1 \text{ } \mu$	3.0	3,330,000	5.5×10^3
1 — $1.5 \text{ } \mu$	1.9×10^7	1,360	5.8×10^{10}
1.5 — $2 \text{ } \mu$	4.0×10^{10}	29	1.5×10^{14}
2 — $2.5 \text{ } \mu$	3.6×10^{12}	3	1.6×10^{16}
2.5 — $3 \text{ } \mu$	7.0×10^{13}	0.71	3.7×10^{17}
3 — $4 \text{ } \mu$	2.4×10^{15}	0.12	1.7×10^{19}

If a photographic plate had a sensitivity in the region of $2 \text{ } \mu$ comparable to that of an ordinary plate in the visual region it would obviously become fogged fairly quickly if exposed to the radiation of a Nernst filament burning at a distance of 29 meters. This demonstrates the practical impossibility of using plates sensitive beyond $2 \text{ } \mu$.

Column 4 gives the number of molecules having a kinetic energy $\frac{1}{2} mv^2$ equal to the quantum $h\nu$ in the various spectral ranges. In principle such a molecule would be able to exert by collision the same effect as a quantum of radiation $h\nu$. The numbers of molecules are 10^3 to 10^4 larger than the numbers of quanta, but the collisional processes may of course be less efficient than the radiative processes.

Table I shows conclusively that there is no hope ever of using photographic plates sensitive beyond $2 \text{ } \mu$.

PASADENA, CALIFORNIA
October 1944