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THE INFRA–RED TRANSMISSION AND REFLECTION OF A NUMBER OF THE ANILINE DYES.

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IN taking up the study of the infra-red tranmission and reflection of the aniline dyes, there are at least two points open for consideration. First the problem of chemical arrangement and optical properties is by no means solved, but rather in its infancy and any new data which may be added to it, will be of service. For the visible spectrum a large amount of data has been obtained, and a number of interesting conclusions have been drawn from them. On the other hand, for the infra-red spectrum there exists a meagre amount of data in comparison to the amount available and anything like a rigorous test of the theory relating chemical arrangement or constitution with absorption has not been possible.

Unfortunately in studying the infra-red properties one is very much restricted in the study, owing to the great opacity of most of the organic substances to the long wave radiation, consequently leading to the use of very small angled prisms and thin films. Thin films and small angled prisms are in many instances impossible to produce and their use when produced is not at all certain, in the study of the infra-red spectrum.

A second point for consideration in the study of these dyes is their reflecting power. The aniline dyes show the property of surface color to a marked extent and it is possible that this property may exist for other wave lengths than those found in the visible spectrum. Associated with the phenomenon of surface color or residual rays, one finds a weak transmission of the wave lengths so reflected. In considering the subject of metallic reflection it must be borne in mind that not all absorption bands or better, bands of weak transmission, correspond to periods of powerful reflection. The so-called absorption bands are not absorption bands in the true sense, for according to the electro-magnetic theory of light at these wave-lengths the energy does not penetrate into the medium upon which it is incident and give rise to heat (true absorption) but owing to the periodic motion of the electrons set up by the incident vibrations,
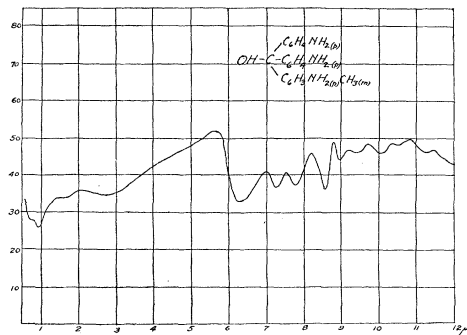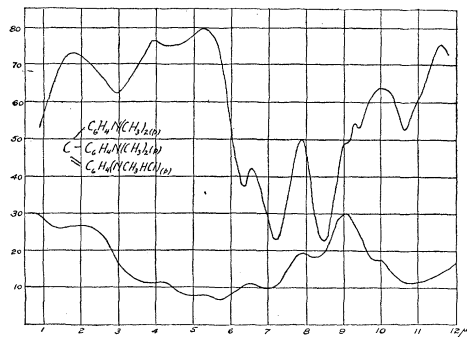
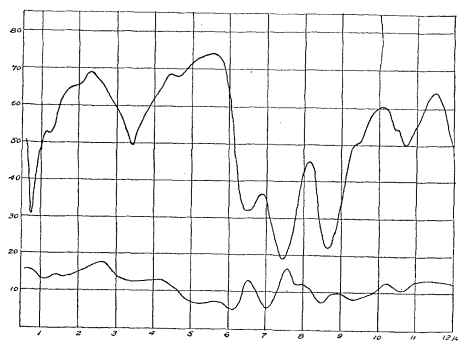Fig. 1.

Rosaniline.

Fig. 2.

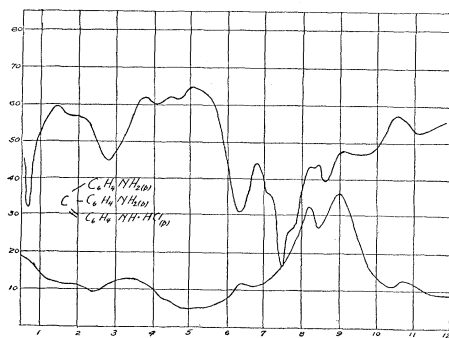Methyl Violet.

Fig. 3.
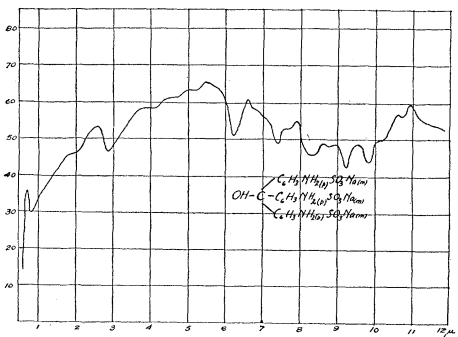
Paris Violet.
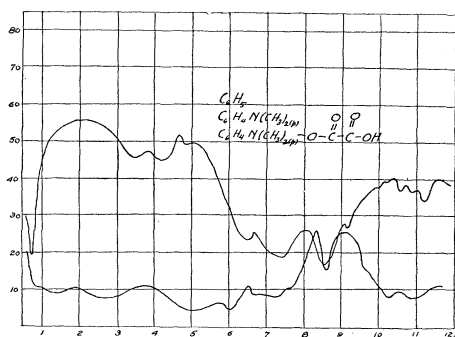
Fig. 4.

Fuchsine.

Fig. 5.

Ruby S.

Fig. 6.

Malachite Green.

resulting in a neutralization of the electric intensity at the surface, the energy will be thrust back into the first medium as reflected energy.

A study of the dyes will not therefore be complete until an investigation of their refractive indices can be carried out for the infra-red region. Pfluger[1] has carried out an investigation of the refractive indices and absorption coefficients of the aniline dyes using very small angled prisms. The problem however dealing with the infra-red region is one of considerably more difficulty owing to the strong absorption of the dyes for the longer waves, and the lack of sufficient sensibility of the infra-red spectrometer.

Experimental Procedure.

The investigation was carried on by means of a specially built spectrometer[2] suitable for measurements in the infra-red region of the spectrum. The energy from a Nernst glower was focused upon the slit of the spectrometer by means of a concave mirror. The image of the slit was then brought to focus upon the thermo-pile after having been subjected to the procedure required by the Wadsworth mounting of the rock salt prism.[3]

The thermo-pile galvanometer combination was the same as that previously described by one of us.[4] The combination possessed a sensibility, such that the energy at the position of the sodium lines in the spectrum gave a deflection of 60 mm. with the galvanometer at a distance of a meter and a half from the galvanometer.

In order to determine the transmission of the dye a thin film of it in the solid state was drawn before the slit of the spectrometer by means of a suitable carriage, thus giving a reduced deflection for the desired wavelength. The ratio of the deflection to the deflection without the dye present gave the transmission of the dye for that particular wave length and thickness of the film.

For the determination of the reflection of the dye a modified procedure was necessary. The energy from the glower was focused upon the film of the dye and this image was in turn focused upon the slit of the spectrometer. The film was spread over a piece of glass and fastened to a sliding carriage which also held a piece of silvered mirror. The carriage was so arranged that the dye could be replaced by the polished silver surface. The ratio of the galvanometer deflection with the dye in position to the galvanometer deflection with the silver surface in place gave the percentage reflection.

The chief difficulty experienced in the work was the production of

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[1] Wied. Ann., *128*, 145, 1899.

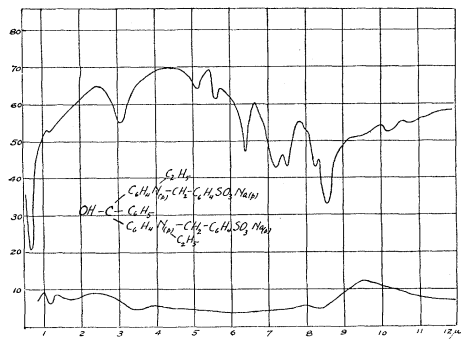[2] Astrophysical Journal, *39*, 243, 1914.

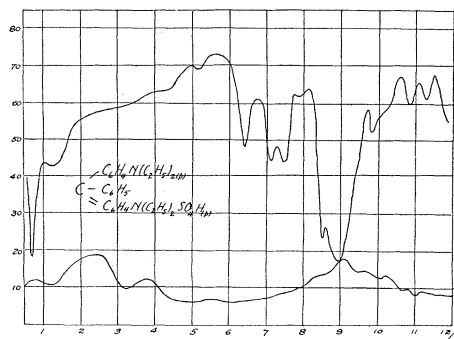[3] Phil. Mag., 38, 1904.

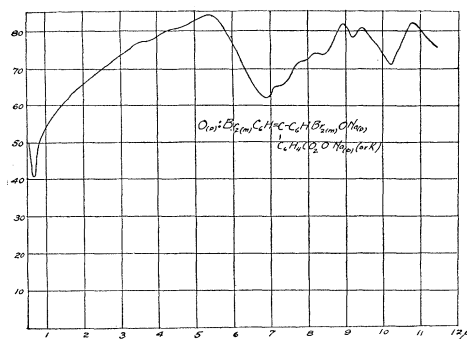[4] *Loc. cit.*

Fig. 7.

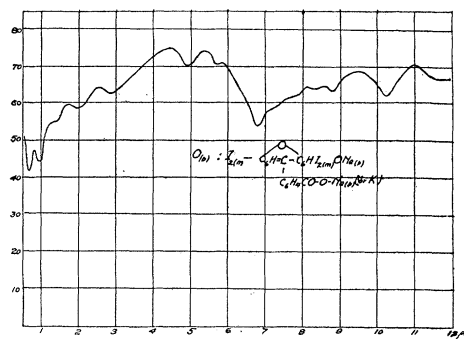Guinea Green.

Fig. 8.
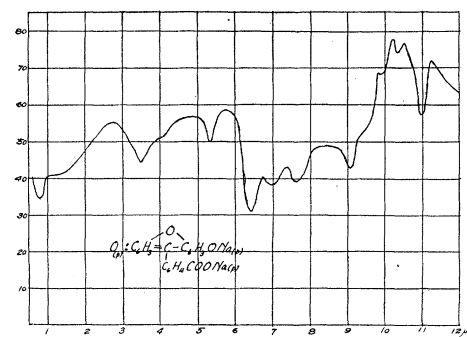
Brilliant Green.

Fig. 9.

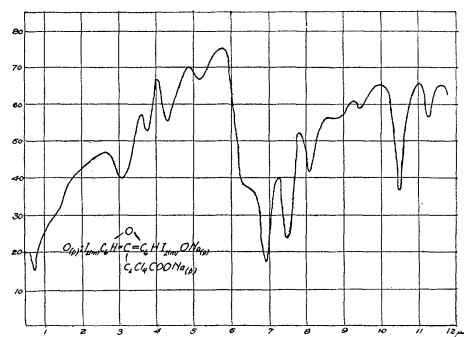Eosine.

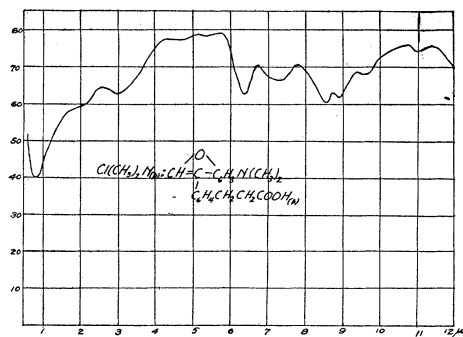Fig. 10.

Bluish Eosine.
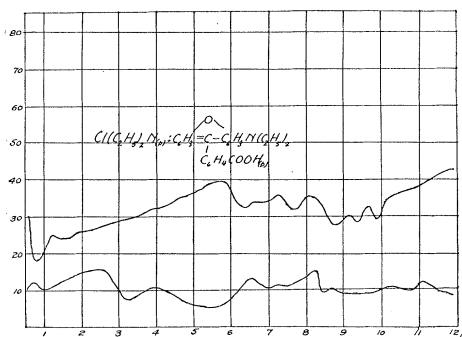
Fig. 11.

Uranine.

Fig. 12.
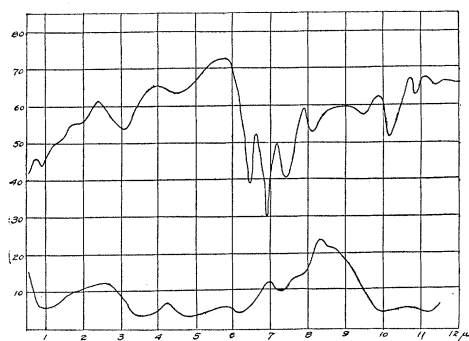
Rose Bengal.

Fig. 13.
Acid Rhodamine.

Fig. 14.
Rhodamine.
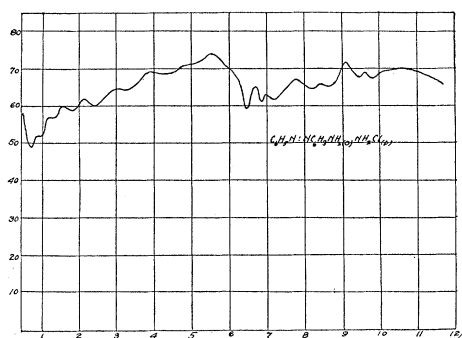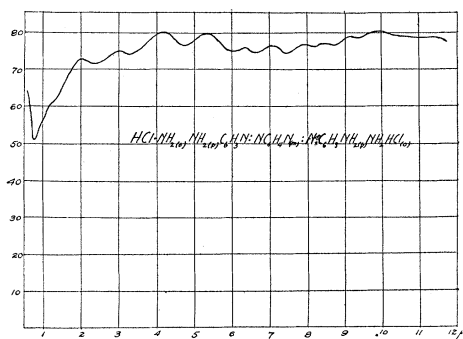
Fig. 15.
Erythrosin.

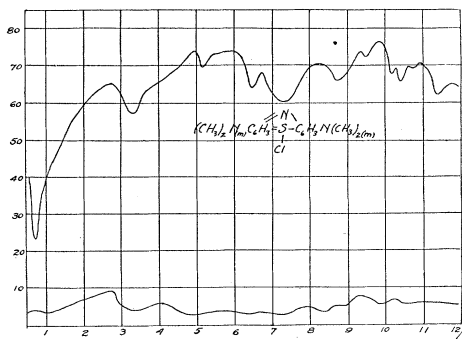Fig. 16.
Chrysoidine.

Fig. 17.
Bismarck Brown.

Fig. 18.
Methyl Blue.

suitable films from the dyes. The dyes were so opaque to the infra-red radiation that it was necessary to spread them over the surface of some diathermaneous medium, in this instance rock salt, in very thin films of thickness perhaps not more than a few wave lengths of visible radiation. The use of the rock salt made the production of the films very difficult, in as much as the only good solvent for the dyes is water. It seemed that no regular procedure could be used: each dye required its own particular treatment. In one or two instances a film was formed by melting the dye, but in most instances the films were obtained from solutions formed in amyl alcohol. Frequently, where solution was possible, films could not be obtained owing to the strong surface tension drawing the dyes up into small irregular patches on evaporation of the solvent. The production of films for reflection was in some instances more difficult, for a film which could be used for transmission was frequently too rough for reflection. Consequently it was impossible to obtain the reflection of all the dyes available. Many dyes which could have been used successfully were not available. It is hoped that the future may make these dyes available.

The chemical constitution of the materials was found in Remsen's Organic Chemistry, in Formanek's work and the greatest number in Greene's tables based upon the work of Drs. Shultz and Julius. The constitution of three of the dyes could not be found in the references and of cyanin and æsculin it is only known that they are a quinoline derivative and a glucoside respectively. The constitution of each substance accompanies its transmission curve.

The results are expressed in the form of transmission and reflection curves. The abscissæ are wave-lengths expressed in μ. The ordinates are per cent. transmission and reflection. Where two curves are plotted on the same coördinate system the lower of the two curves is the reflection curve.

The accuracy of the wave-length determination for the transmission curves is about .05 μ with the exception of the wide flat bands of very low transmission where the error is slightly greater. The error for the reflection curves is slightly greater than .05 μ, owing to the small amount of energy reflected corresponding frequently to not more than two or three millimeters galvanometer deflection.

Considering first the transmission curves with reference to the chemical constitution of the substances, a few points of interest are to be noted. There is a general similarity in all of the curves. All have one or two bands in the extreme red end of the visible spectrum causing in part the color of the substance. There is then a region comparatively free from absorption with a maximum of transmission in the region of the wave-
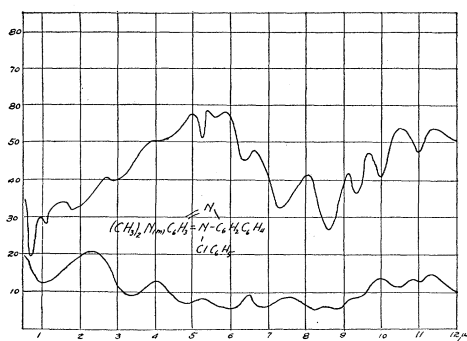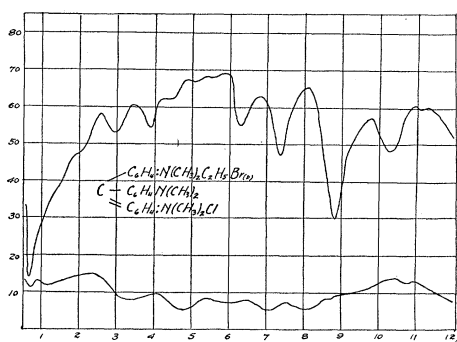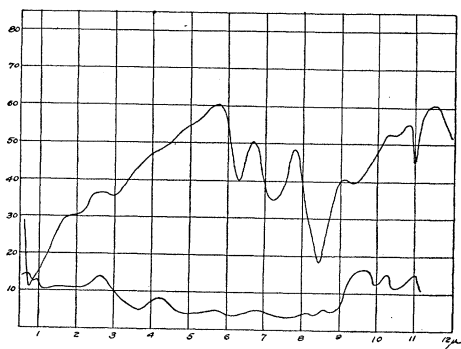
Fig. 19.
Neutral Blue.

Fig. 20.
Methyl Green.

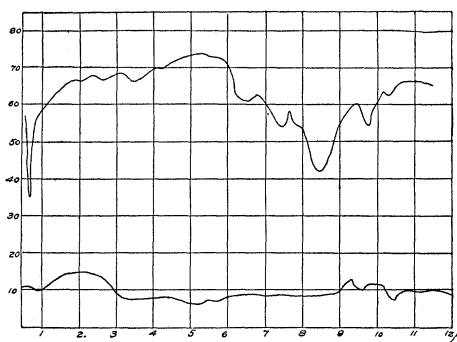

Fig. 21.
Cyanile Green.

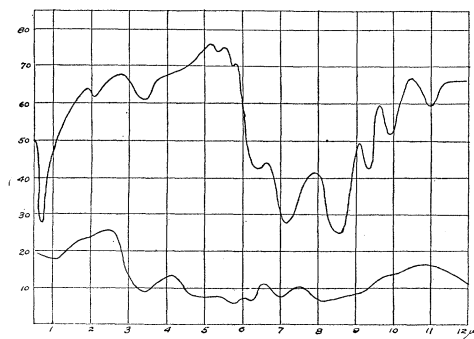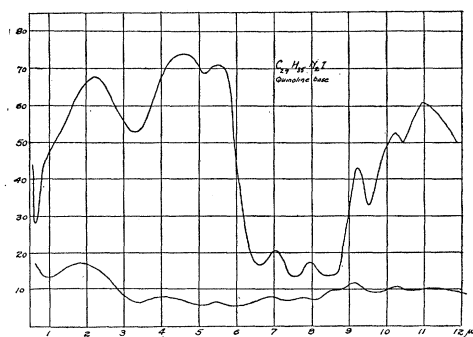Fig. 22.
Neptune Green.

Fig. 23.
Steel Blue.

Fig. 24.
Cyanine.

length 5.5 μ.   From this point on there is, in most cases, a sudden drop in transmission and then a region of complex absorption takes place to about the wave-length 9.0 μ, where the transmission again increases with or without bands.

In the region of complex absorption before 9.0 μ a higher dispersion would have revealed perhaps a large number of narrow deep bands. Further are to be noted the three deep bands in the interval between 6.0 μ and 9.0 μ of the triphenyl methanes and the triphenyl carbinols, and it would seem that the three substances of unknown composition, cyanile green, neptune green and steel blue, belong to these classes.   The rosamine and quinoline substances show bands in this region but less accentuated.   The substances named methyl violet and Paris violet are given as identical in composition as is also the case with eosine bluish and erythrosine.   Their curves show differences in the disposition of the bands of minimum transmission.   This may be due to impurities for it is very difficult to obtain dyes of guaranteed purity, or the differences shown
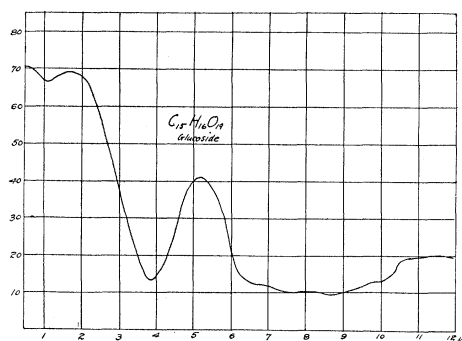
Fig. 25.

Aesculin.

may be in reality due to the differences in chemical arrangement which have not been noted chemically.

Striking differences from the work of other observers appear in the transmission curves.   Coblentz gives a list of bands assigned to different groups in the molecule as found by himself and others.   The band at 3.42 μ ascribed by Julius to the CH_3 group occurs in but five of the curves, figs. 3, 6, 11, 17 and 24, two of which have the CH_3 group substituted in the amine group, two have no CH_3 groups and the fifth is unknown.   The benzene ring is the next most prominent structural feature of these compounds but only two of the curves show a band at 3.25 μ, one has the 6.75 μ band and none the bands at 9.8 μ or 11.8 μ and but few the band at or near the wave-length 8.68 μ.

At least sixteen of the substances contain the OH or the NH$_3$ groups yet only five curves have the band at 2.95 μ, while none of them have the band at 6.1 μ.   On the other hand, acid rhodamine is the only substance examined having the chlorine atom in the ring.   It shows the band at 4.30 μ ascribed to chlorine.

From such conflicting data it is difficult to draw conclusions.   The theory that certain chemical groups give rise to definite bands of minimum transmission certainly does not appear applicable to such complex substances.   The large amount of evidence which seems to support the theory comes largely from a study of substances of fairly simple structure, but even with these substances the theory has a good many qualifications. With the more complex substances various constraints between the groups may well alter the position of the bands corresponding to them· However under these conditions it can not be said that to a certain chemical group there corresponds an absorption band at a definite wavelength.

REFLECTION.

The reflecting power of the dyes is generally small.   The films from which the reflection was obtained were very thin.   This should however make no difference in the reflection since the phenomenon sought is a surface one.   There is however the possibility that the body color of the dye might make its appearance in the reflection curves but this would be fairly easy to detect for in general the body color obtained from the reflected light would correspond in position with the color shown on transmission.

A study of the reflection curves shows us that in a few instances there is comparatively strong reflection.   It however is not of the intensity of metallic reflection.   In some instances these maxima correspond to a minimum of transmission.   Brilliant green shows a maximum of reflection corresponding to a weak transmission at the wave-length 9.0 μ. Erythrosine shows a maximum of reflection at 6.8 μ corresponding to a sharp minimum of transmission.   A further increase of the reflecting power takes place beyond that wave-length corresponding to a rather complicated transmission from which it is difficult to draw definite conclusions.   Paris violet shows strong reflection at 6.5 μ and 7.6 μ corresponding to weak transmission.   Fuchsine shows a weak maximum of reflection at 6.4 μ corresponding to small transmission.   Steel blue shows a broad reflection at the wave-length 8.5 μ corresponding to weak transmission at that point.   It is also to be noted that erythrosin possesses a broad band of reflection at 9.4 μ corresponding to complicated transmission.   Methyl violet possesses similar characteristics in the region of

10 μ. Likewise malachite green in the region of 9.5 μ. Whether any of the bands of reflection may be classed as residual rays seems rather doubtful, owing to the small value of the reflection coefficient. The method of multiple reflection would in all probability answer the question in the negative. There is one characteristic which nearly all of the dyes show on reflection. One notes on examining the curves that they reflect relatively well to the wave-length 2.8 μ where there occurs a sudden drop to a value of the reflection coefficient of a few per cent. The transmission curves are characterized by a weak transmission at the wave-length 3.0 μ rising to a maximum again rather suddenly. The reflection curves do not rise to a maximum immediately.

CONCLUSIONS.

The reflection and transmission of a number of aniline dyes have been obtained for the infra-red region of the spectrum to the wave-length 12 μ, thus adding more data to the problem of chemical constitution and absorption.

There is a similarity in the transmission curves for related compounds.

The theory that certain chemical groups in the molecule give rise to definite absorption does not hold with any degree of consistency for these complex substances.

The bands of maximum reflection in general coincide with periods of weak transmission. The evidence furnished does not seem to be conclusive in determining whether or not these are bands of metallic reflection. In all probability they are not.

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