

or salts are the means by which these stimulations are brought about, as suggested in my ion-protein theory and by the investigations of Lasareff.

<sup>1</sup> Loeb, *The dynamics of living matter*, New York, 1906. *Physiologische Tönenwirkung, Oppenheimer's Handbuch*, Vol. 2, Jena, 1909.

<sup>2</sup> Loeb, *Amer. J. Physiol.*, 3, 434 (1899); 6, 411 (1902); and *J. Biol. Chem.*, 1, 427 (1906).

<sup>3</sup> Lasareff, *Arch. ges. Physiol., Bonn*, 135, 196 (1910).

<sup>4</sup> Lasareff, *Arch. ges. Physiol., Bonn*, 154, 459 (1913).

<sup>5</sup> Loeb, *Science*, 40, 316 (1914); *Amer. Nat., Boston*, 49, 257 (1915).

## THE POLARIZED FLUORESCENCE OF AMMONIUM URANYL CHLORIDE

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The remarkable fluorescence spectrum of ammonium uranyl chloride ( $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ ), which has been described in a recent paper read before the American Physical Society, consists of several equidistant

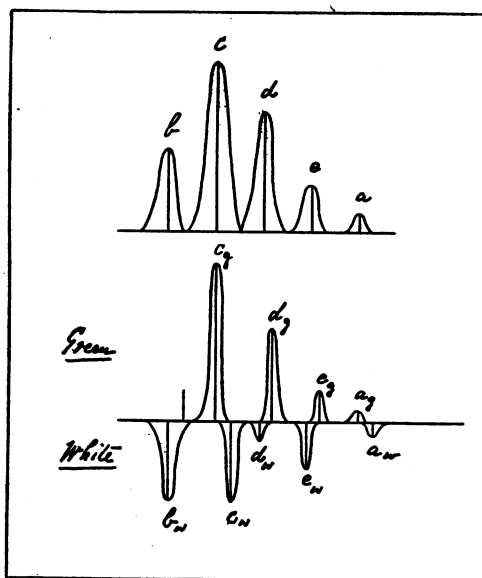


FIG. 1

groups of bands. Each group contains five nearly equidistant bands, *b*, *c*, *d*, *e*, and *a* (fig. 1) and the spacing repeats itself with such precision in successive groups that the homologous bands,  $b_1, b_2, b_3, \dots, c_1, c_2, c_3$  (see fig. 2) form series having a common and constant frequency interval.

Observations at the temperature of liquid air show that these bands are really doublets, unresolved at  $+20^\circ$  but separated at low temperatures; a dim companion of the band as observed at  $+20^\circ$  increasing greatly in brightness as the temperature

falls while the dominant member becomes relatively feeble or in some instances disappears altogether. At low temperatures, as is usual with the uranyl compounds, all the bands are very narrow so that overlapping components which are entirely indistinguishable at the tempera-

ture of the room appear as separate bands. The relative brightness of the components, and also the effect of temperature upon them, varies greatly with different bands.

Ammonium uranyl chloride crystallizes in triclinic plates, some of which show a marked pleochroism. According to Mr. D. T. Wilber, to whom we are indebted for the preparation of this and the other uranyl compounds mentioned in this paper:

The strong pleochroism is observed in crystals tabular parallel to the face  $c(001)$  the crystals being set to correspond with the isomorphous potassium uranyl chloride as described in Groth's *Chemische Krystallographie*, volume 1, p. 594. The transmitted light is polarized with one component vibrating nearly parallel to the edge between the  $c(001)$  face and the  $b(010)$  face. This is less absorbed, the transmitted light appearing nearly white in

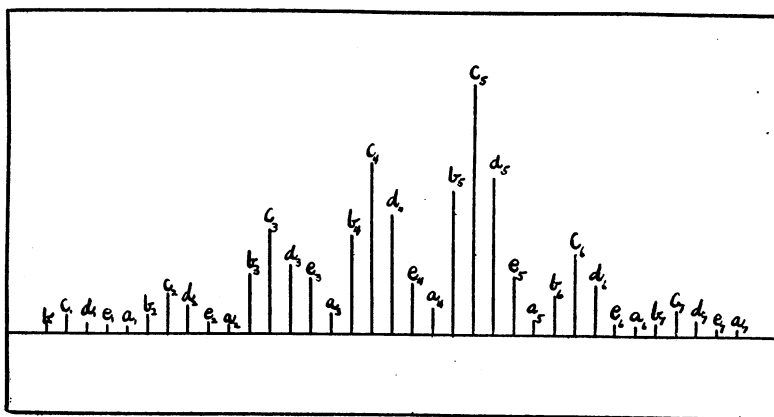


FIG. 2

plates 1 mm. or less in thickness. The component at right angles to this is strongly absorbed in the blue and violet and appears deep greenish yellow even in much thinner layers.

We shall designate these directions of polarization simply as *white* and *green*.

When the violet rays from an electric carbon arc are transmitted through the slit of a spectroscop and the fluorescence and absorption bands are observed through a Nicol prism, marked changes are found to occur as the Nicol is turned with its plane polarization parallel successively to the green and white planes of the crystal.<sup>1</sup>

The two components of the fluorescence and absorption may be conveniently observed simultaneously by means of the following arrangement of apparatus which is that employed in our determinations.

In the collimator of a spectroscope a doubly refracting rhomb was so mounted as to give vertically displaced images of the slit, and the length of the slit was adjusted so as to render these images contiguous but not overlapping. Two spectra one above the other were thus produced polarized vertically and horizontally and when the crystal to be studied was mounted before the slit and carefully adjusted by rotation until its planes of polarization were likewise vertical and horizontal these spectra gave the fluorescence and absorption for the *green* and *white* components respectively. A suitable light filter of deep blue glass which was opaque to the entire region occupied by the fluorescence so that the bands appeared upon a black background was placed in the path of the incident light. It transmitted light of the wave-lengths necessary to excitation, however, and this included the region of the absorption spectrum, so that fluorescence bands and absorption bands were simultaneously visible in both spectra.

Complete separation of the two polarized components, even when the adjustments are accurately made, occurs only when the crystal is perfect and many specimens were tested and discarded before one suitable for study was found. The best results were obtained with small thin crystals newly formed and immediately protected from the air by a layer of Canada balsam.

Comparisons of the fluorescence bands by the method just described show that in the various groups each band consists of two components; thus confirming in general the conclusions reached by the study of the unpolarized fluorescence at  $+20^{\circ}\text{C}$ . and  $-185^{\circ}$ . These components moreover are polarized at right angles to each other. The stronger fluorescence, as might perhaps be expected, is polarized in the *green* direction, corresponding with the greater absorption.

The location and roughly approximate relative intensity of the fluorescence of each group is indicated in figure 1, in which for a single typical group the bands of the unpolarized spectrum are shown and, below, the *green* and *white* components. From this figure it will be seen that all except the band *b* appear as oppositely polarized doublets. This band in the *green* spectrum is absent or too dim for detection. We know however that at  $-185^{\circ}$  a component at the position *b'* takes the place of *b* hence it is probably only a question of insufficient brightness. The component *d<sub>w</sub>* is so dim as to be seen only with great difficulty and the same is true of *a<sub>w</sub>*.

For purposes of measurement photographs were made of the spectra of this compound and also of the fluorescence and absorption of crystals of potassium uranyl chloride, caesium uranyl chloride, and rubidium

uranyl chloride prepared for us by Mr. Wilber. In photographing absorption bands a nitrogen filled tungsten lamp was substituted for the arc and a light blue filter was sometimes used in place of the deep blue screen already described. Owing to the very great range of intensity in the fluorescence bands and the great difference in the transmission, within the region of absorption for the *white* and *green* directions respectively it was necessary to make many exposures of varying duration in order to obtain a complete record of the spectra.

When the transmitted light is polarized and parallel to one of the planes of vibration of the crystal, only one absorption spectrum is observed and the completeness of extinction of the other affords a delicate test for the adjustment of the apparatus and for the homogeneity of the specimen. It is however significant that the two polarized fluorescence spectra are always present, provided the emission is that leaving the

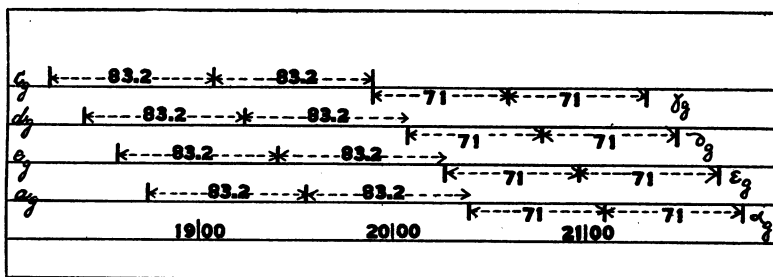


FIG. 3

crystal in the direction described in an earlier paragraph, and these spectra are the same whether the exciting light is polarized in the *white* or the *green* direction or whether unpolarized light is used for excitation. The exciting light, moreover, may enter the crystal in any direction without affecting the character of the fluorescence spectra.<sup>2</sup>

This is in accord with the general principle established by the study of numerous cases of fluorescence,<sup>3</sup> i.e., that a fluorescence band is independent, as regards its location and character, of the nature of the excitation.

It follows moreover that a beam of plane polarized light is capable of exciting not only the polarized fluorescence which has its vibration in the same plane *but likewise that component of the fluorescence which is polarized at right angles to the exciting light*. This would seem to remove the fluorescence of these crystals and presumably the very similar fluorescence of the other uranyl compounds from the class designated by Wood as resonance spectra.

The absorption spectrum of ammonium uranyl chloride, observed under the conditions described above, is no less remarkable than the spectrum of the fluorescent light.

It extends from just about  $0.5 \mu$  into the ultraviolet and consists, like the fluorescence spectrum, of several series of equidistant bands having a common frequency interval.

This interval, expressed arbitrarily in the form  $10^3/\lambda$  where  $\mu$  is the unit of wave length, is approximately 71.0 whereas the interval for the fluorescence is 83.2.

Our earlier observations, without regard to polarization had led to the recognition of four series designated as  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and three of these appeared to consist of doublets.

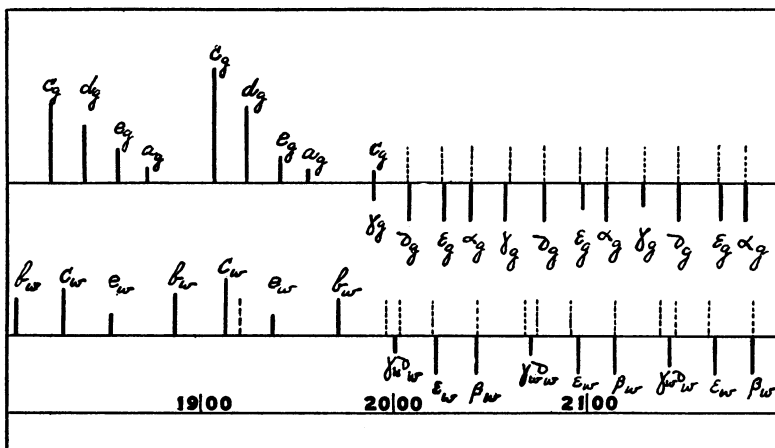


FIG. 4

The relation between absorption and fluorescence at  $+20^\circ$  is briefly as follows:

In the region lying between  $0.5075\mu$  and  $0.4900\mu$  which is occupied by the fluorescence group of shortest wave length, and which we have termed the reversing region, there is an absorption band for each fluorescence band and coincident as to position. The reversing region is the most unsatisfactory for the study of fluorescence on account of this coincidence of fluorescence and absorption. It is however possible by the use of suitable screens, to almost entirely suppress fluorescence and to locate the absorption bands of this region. Towards the red all the fluorescent bands form series with a common constant interval of 83.2. Towards the violet all the absorption bands belong to similar series starting from these reversible bands with a common constant interval of 71.0. (See fig. 3.)

If these remarkable relations are fundamental rather than fortuitous they should be found to exist where the spectra are resolved into their polarized components: i.e., the absorption spectrum of each component should consist only of series corresponding to the several fluorescence series of that component and each series of the fluorescence spectrum should have its related series of absorption bands. The rigorous test is difficult because of the incomplete separation of the components in most crystals. That the relation holds however with slight discrepancies, obviously ascribable to the necessarily imperfect conditions as regards polarization, will be seen from figure 4.

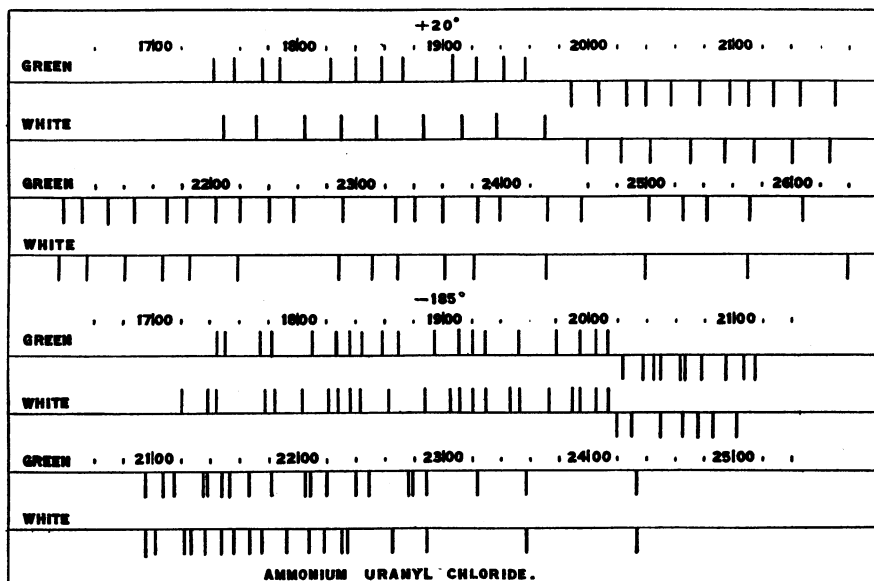


FIG. 5

In this diagram the reversing region, together with two groups of fluorescence bands, to the left, and of absorption bands to the right, is shown for the green and white components of the spectrum. The location of fluorescence bands is indicated by solid vertical lines above the base line, absorption by lines below. Fluorescence is designated by  $b_g, c_g, d_g, e_g, a_g$  for the green component and  $b_w, c_w, d_w, e_w, a_w$  for the white component. The absorption series related to the above are marked  $\beta_g, \gamma_g, \delta_g, \epsilon_g, \alpha_g$ , and  $\beta_w, \gamma_w, \delta_w, \epsilon_w, \alpha_w$  respectively.

It will be noted that each series of the green component has its properly related absorption series and that no other absorption bands occur; also that  $b_g$ , which is absent or too weak to be observed, is not represented by a related absorption series. The same is true of the

white component excepting that the closely neighboring and feeble  $\gamma_w$ , and  $\beta_w$  are blended into a single intermediate band in each group. The  $\epsilon_w$  series moreover is slightly shifted towards the violet. The positions given are the averages from five of seven negatives measured.

In figures 3 and 4 only the groups near the reversing region have been indicated. Figure 5 shows all the bands thus far located in the polarized spectra of ammonium uranyl chloride. The diagram is by no means complete however for in the previous studies of the spectrum of this salt, already referred to, at least seven groups of fluorescence bands and eight groups of absorption bands were found. Preparations are in hand for extending the study of the absorption spectra into the ultra violet by means of a quartz spectrograph.

Analogous relations between the two components of the fluorescence and absorption spectra of the other three uranyl double chlorides,  $2\text{KCl} \cdot \text{UO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ ;  $2\text{RbCl} \cdot \text{UO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$  and  $2\text{CsCl} \cdot \text{UO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$ , have also been determined. Full data concerning these spectra and that of the ammonium uranyl chloride at  $+20^\circ$  and  $-185^\circ$  will be published at an early day.

<sup>1</sup> Polarized fluorescence, first described by Grailich (*Krystall-optische Untersuchungen*, Wien, 1858) has since been studied by Maskalyne (*London, Proc. R. Soc.* 28, 479), V. Lommel (*Ann. Physik., Leipzig*, 8, 634), E. Wiedemann (*Ibid.*, 9, 158), Sohncke (*Ibid.*, 58, 417); G. C. Schmidt (*Ibid.*, 60, 740), and H. Becquerel, (*Paris, C. R. Acad. Sci.*, 144, 671).

<sup>2</sup> Becquerel, in the paper already cited, has noted the fact that the fluorescence spectrum is not changed by polarizing the incident light. Sohncke obtained a similar result with calcite and some other crystals but found certain exceptions to the general rule.

<sup>3</sup> See Nichols and Merritt, *Physic. Rev.*, Ser. 1, 27, 373 (1908); also *Studies in Luminescence*, Carnegie Institution (1912).

## THE LINGUISTIC CLASSIFICATION OF POTAWATOMI

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For a considerable period of time it has been commonly supposed that Potawatomi is very closely related to Ojibwa and Ottawa. The statement of William Jones in his *Some principles of Algonquian word-formation*<sup>1</sup> is the most authoritative one on this point. In my *Preliminary report on the linguistic classification of Algonquian tribes*<sup>2</sup> I concluded from my limited first-hand knowledge of Potawatomi that Potawatomi belonged to the Ojibwa group (comprising Ojibwa, Ottawa, Algonkin, Potawatomi; and somewhat removed from them Peoria, etc.) of Central Algonquian dialects, but that Potawatomi differed more from Ojibwa, Ottawa, and Algonkin than these from one another. But