

ANALYSIS OF THE ABSORPTION AND FLUORESCENCE
SPECTRA OF URANYL SALTS.

(PART I.) URANYL ACETATE (ABSORPTION)

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ABSTRACT. The absorption spectrum of uranyl acetate was analysed as consisting of two systems involving two transitions from two excited states to a common ground state. The separation between these two excited states was found to be ν 1839 cm^{-1} or 0.228 e.v. System I was explained on the basis of a (0,0) band at ν 20589 cm^{-1} and two upper state fundamentals 735 and 36 cm^{-1} and three lower state fundamentals 856, 210 and 30 cm^{-1} . System II was explained on the basis of a (0,0) band at ν 22428 cm^{-1} and the upper state fundamentals 711 and 212 cm^{-1} and the ground state fundamentals 841 and 228 cm^{-1} .

INTRODUCTION

The spectroscopic properties of uranyl salts have been investigated by a large number of workers from time to time. Significant experimental work has come from Nichols and Howes (1919) on both fluorescence and absorption spectra with some suggestions on the regularities in the spectra. Van Heel and Dieke (1925) suggested that the bands arise out of electronic-vibrational transitions in the uranyl radical. Further attempts by Van Heel (1925) for a detailed interpretation were not of much significance. The study of Raman and infrared spectra by Conn and Wu (1938) and Satyanarayana (1942) established three fundamental frequencies in the ground state 860, 930 and 210 cm^{-1} and a bent structure for the uranyl radical (c_{2v} point-group). Pant (1945), analysed the fluorescence spectra of some simple uranyl salts and arrived at the conclusion that the bands arise out of a transition from a single upper electronic state to vibrational levels in two closely lying lower states. Freymann etc. (1946) carried out analysis of uranyl acetate bands and interpreted them as involving only two states. In 1949, Dieke and Duncan have published an extensive report on the spectroscopic properties of uranium compounds in which we do not find some simple uranyl salts like acetate. In 1950, Pant published the analysis of some uranyl salts on the same lines, as in his analysis of the fluorescence bands. He disputed the analysis of Van Heel and Freymann etc. on various experimental grounds. In view of the extremely controversial nature of the analyses of the various workers mentioned above, it was felt worthwhile to investigate these spectra thoroughly and independently, using our own experimental data. Investigations were made on the absorption spectra of uranyl acetate and uranyl nitrate and the data were compared with those of Nichols and Howes, those of Freymann and also those due to Dieke and Duncan (nitrate). We find that our data, in general, are in good agree-

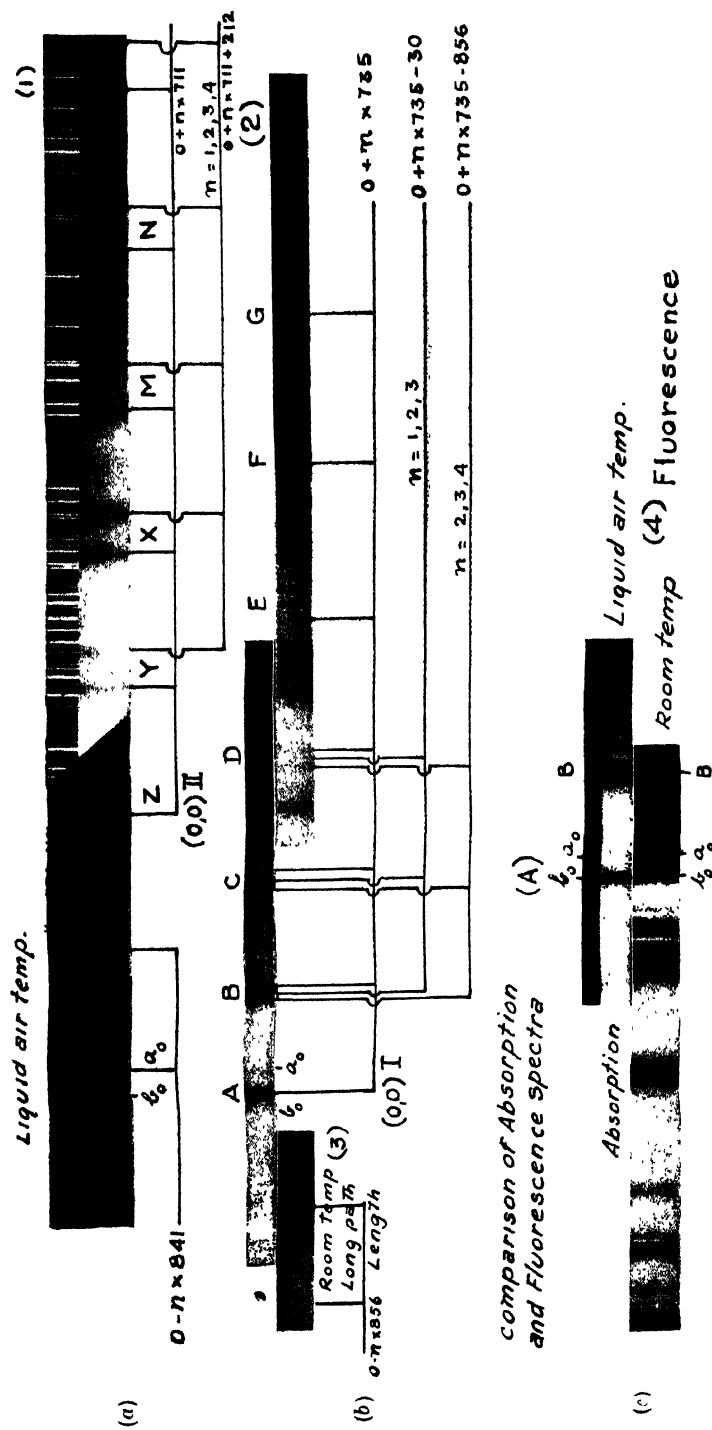


Fig. 1. Absorption spectrum of uranyl acetate.

ment with those of Nichols and Howes and of Dieke and Duncan. The values of Freymann and others are generally found to be slightly higher than ours.

The analysis of these bands has been attempted mainly depending on the features like grouping, intensities, and sharpness of the bands. It is well known in the near ultraviolet absorption spectra of the aromatic molecules, the pattern of the bands plays an important role in the analysis. As a result of this effort on our part, we analysed these bands into two systems, the one with a (0,0) at ν 20589 cm^{-1} and the other (0,0) at ν 22428 cm^{-1} with the possibility of a common ground state. The analysis and its justification and the reasons for our preference of our analysis over others are presented below.

EXPERIMENTAL

Absorption spectra are taken at the liquid air and room temperatures with a variety of path-lengths.

The experimental set-up consists of a brass rod with a rectangular slot in the middle, in which a small glass cell containing the salt is placed tightly. The cell is made of two small rectangular glass plates cut to the size of the slot. Two small holes are bored in the rod at the middle of the slot, one to allow the incident light and the other the transmitted light. The source of continuum is 1000 watt tungsten lamp. The brass rod is suspended by means of a wire into liquid air contained in a transparent Dewar flask. The spectrum is photographed with the help of a Fuess spectrograph (24 A.U. per m.m. at λ 4500) using Ilford Selochrome and Panchromatic plates.

The fluorescence spectra, for the present, are taken only at the room temperatures. Mercury arc was used for the excitation.

Description of the bands (figure 1)

It is well known that the bands of the uranyl salts appear sharp and distinct only at low temperatures. In figure 1 (a), the bands obtained at the liquid air temperature with one path length, are shown. To facilitate description, arbitrary markings like A, B, C, D... and Z, Y, X, M... are adopted. Band A can be seen from figure 1(b) to be a sharp intense band, followed by equally intense bands at B, C, D (see also microphotometer curve in figure 2). These bands B, C, D, on their long wavelength side, are accompanied by two satellite bands which are of much less in intensity. This triplet pattern repeats itself upto D conspicuously. It is not easy to follow this pattern beyond D but at F, on very close examination and at E and G also, on still closer examination, the pattern could be found. What is more conspicuously important in this region is the doublet structure of two broad and diffuse bands marked Y, X, M and N. Their appearance is distinctly different from that of the bands in A, B, C, D. They also definitely resemble the single band at Z which, abruptly presents itself as we study from A, B, C etc. These points are considered to be of much significance

for the analysis. On the longwave length side of A in figure 1(a) there is a definite indication of an abrupt discontinuity in intensity which may be suspected as due to faint absorption. This was established by studying the development of this band at higher temperatures and longer path lengths. Figure 1(b), obtained under

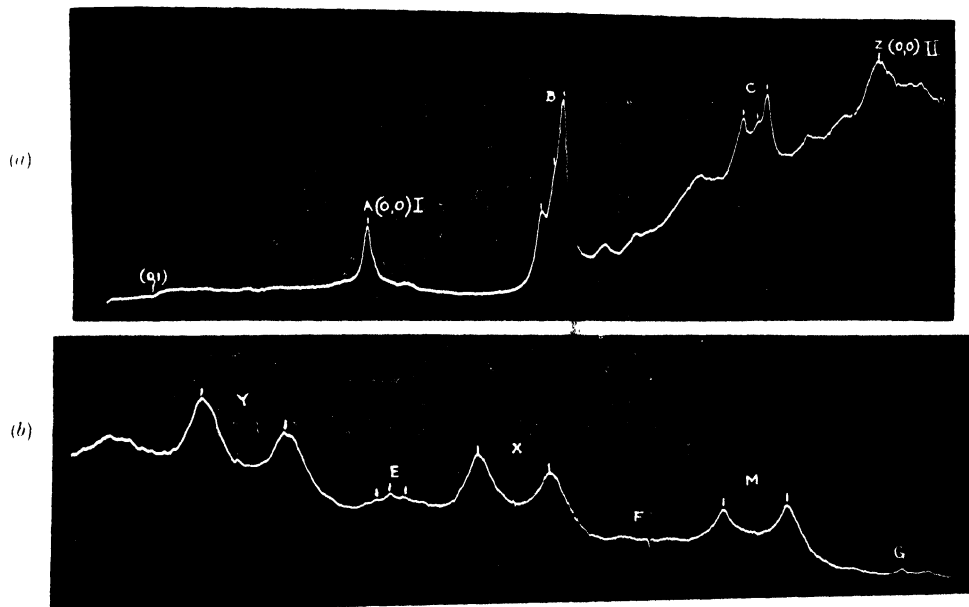


Fig. 2. Microphotometric records of the absorption spectrum of uranyl acetate.

such conditions, definitely establishes this band. A trace of still another band on the long wavelength side of this band is marked in figure 1(b) and it is also found on the negatives corresponding to figure 1(a). The presence of these two bands is of very great importance in the analysis of the spectrum.

In figure 1(a) two bands are marked b_0 and a_0 adopting the nomenclature of Pant. Pant's b_0 is our band A. Between A and B, B and C, and C and D, there are a few weak and diffuse bands which do not form any conspicuous pattern. However, the band a_0 (Pant's terminology) is of crucial importance in our discussion.

In figure 1(c), we have given the fluorescence and absorption spectra side by side taken on the same instrument and to the same scale of enlargement. Earlier authors have reported only four groups of bands in fluorescence starting from ν 20728 cm^{-1} and extending to the long wavelength side. The common region between fluorescence and absorption was only three bands according to earlier workers. They are ν 20746 cm^{-1} , 20625 cm^{-1} and 20587 cm^{-1} in absorption and ν 20732 cm^{-1} , 20627 cm^{-1} and 20588 cm^{-1} in fluorescence. Our picture shows clearly one more group to the short wavelength side obtained on a heavily

exposed plate (exposure 7 hrs.) and this falls in the region of our earlier mentioned B bands. This additional experimental information, we consider, is of great significance in the analysis of the spectra. Detailed work on the fluorescence spectra at various temperatures, is still in progress.

Considerations for the analysis.

It is necessary to examine the reasoning behind the analyses of the earlier workers. Freymann started with the band marked a_0 as the (0,0) and the one marked b_0 (our A) as the (1, 1) transition. He identified a fundamental 720 in the upper state with a similar weak band coming after B and similar bands as the overtones. The strong band b_0 taken as the (1,1) of this frequency and its counterpart in the ground state led to the assignment of similar strong bands as such combination bands. This ultimately led him to the assignment of all strong bands as multiple combinations of various fundamentals in the upper and lower states, the weak bands forming the progression of fundamental 720 (see column 6 of Table I). This is really peculiar and unusual. Besides, his data do not show the bands on the long wavelength side of A while A itself was taken by him as the (1,1) band. This came in for criticism, by Pant on the ground that while the fundamental was itself not found, the difference frequency was found with a very high intensity. In essence, Freymann etc. analysed all the bands as due to one system. Freymann's analysis is conspicuous by the absence of an assignment for the band Z. He gives a wave number of $\nu 22444 \text{ cm}^{-1}$ for this band. Our measurements give an average value of $\nu 22428 \text{ cm}^{-1}$ which agree closely with the value $\nu 22425 \text{ cm}^{-1}$ given by Nichols and Howes. It has already been pointed out that Freymann's data are in general higher than ours and also of Nichols and Howes. So, in the absence of any other band in the neighbourhood of these values, there is no doubt that these two measurements represent the same band which is a very important band. The fact that it does not find an interpretation in Freymann's analysis deserves serious consideration. Besides the above points, we also observe that about five bands in the violet have not been interpreted by them (see Table I, column 6) and the deviations between their observed and calculated values are considerable.

In the analysis of the fluorescence bands, Freymann started with the band a_0 (of Pant) as the (0,0) consistent with his absorption analysis. It is seen that this band is weak in fluorescence as well [figure 1(c)]. Further if we take this band as the (0,0), the new band at B obtained in fluorescence by us and shifted by about 557 cm^{-1} cannot be interpreted in any reasonable manner. This band actually falls in the region of B in absorption, so that, the interpretation of B and this must be identical. We are inclined to consider this as a conclusive evidence against Freymann's analysis.

Pant's analysis was based upon what he considers as experimental facts. The fact that the fluorescence bands are independent of the exciting radiation

TABLE I
Analysis

| Wavenumber of the band cm^{-1} | Intensity | System I | System II | Deviation from the observed values cm^{-1} | Freymann etc. | Deviation from their observed values cm^{-1} | D. D. Pant | Deviation from their observed values cm^{-1} |
|---|-----------|---------------------------------------|------------------------------|---|---|---|--------------------------------|---|
| 18855 | 1 | $0-2 \times 856 = 18877$ | | 22 | | | | |
| 19733 | 2 | $0-856 = 19733$ | | 0 | | | | |
| 20589 | 8 | (0,0)I | | 0 | $0-860+720=20616$ | 23 | $b_0(0,0)$ I = 20593 | 0 |
| 20625 | 1 | $0+36=20625$ | | 0 | | | | |
| 20750 | 2 | | $0-2 \times 841 = 20746$ | 4 | (0,0) = 20756 | 0 | $a_0(0,0)$ II = 20756 | 0 |
| 20823 | 1 | $0+36+212 = 20837$ | | 14 | $0+2 \times 720-930-2 \times 210 = 20846$ | 22 | $b_0+220 = 20813$ | 11 |
| 20891 | 1 | $0+735-2 \times 210 = 20904$ | | 13 | $0+2 \times 720-2 \times 210-860 = 20916$ | 13 | $a_0+220 = 20976$ | 73 |
| 21242 | 6 | $0+2 \times 735-856 = 21203$ | | 39 | $0+2 \times 720-930 = 21266$ | 16 | $a_0+725-235 = 21246$ | 4 |
| 21293 | 4 | $0+735-30 = 21294$ | | 1 | | | | |
| 21324 | 10 | $0+735 = 21324$ | | 0 | $0+2 \times 720-860 = 21336$ | 11 | $b_0+725 = 21318$ | 3 |
| 21477 | 2 | | $0-2 \times 841+711 = 21437$ | 20 | $0+720 = 21476$ | 17 | $a_0+725 = 21481$ | 12 |
| 21587 | 2 | | $0-841 = 21587$ | 0 | $0-3 \times 720-930-2 \times 210 = 21566$ | 18 | $b_0+725+220 = 21538$ | 46 |
| 21641 | 1 | $0+2 \times 735-2 \times 210 = 21639$ | | 2 | $0-3 \times 720-2 \times 210-860 = 21636$ | 21 | $a_0+725+220 = 21701$ | 44 |
| 21822 | 2 | $0+2 \times 735-210 = 21840$ | | 27 | $0+3 \times 720-210-860 = 21846$ | 20 | | |
| 21963 | 6 | $0+3 \times 735-856 = 21938$ | | 25 | $0+3 \times 720-930 = 21986$ | 42 | $a_0+2 \times 725-235 = 21971$ | 4 |
| 22022 | 3 | $0+2 \times 735-30 = 22029$ | | 7 | | | | |
| 22053 | 8 | $0+2 \times 735 = 22059$ | | 6 | $0+3 \times 720-860 = 22056$ | 13 | $b_0+2 \times 725 = 22043$ | 0 |
| 22200 | 2 | | $0-228 = 22200$ | 0 | $0+2 \times 720 = 22196$ | 11 | $a_0+2 \times 725 = 22206$ | 1 |
| 22307 | 2 | | $0-841+711 = 22298$ | 9 | $0+4 \times 720-930-2 \times 210 = 22286$ | 18 | $b_0+2 \times 725+220 = 22263$ | 41 |
| 22428 | 8 | | (0,0) II | 0 | | | $a_0+2 \times 725+220 = 22426$ | 18 |

TABLE I (contd.)

| Wavenumber of the band cm^{-1} | Intensity | System I | System II | Deviation from the observed values cm^{-1} | Freymann etc. | Deviation from the observed values cm^{-1} | Pant | Deviation from their observed values cm^{-1} |
|---|-----------|--------------------------------|--------------------------------|---|---|---|---|---|
| 22578 | 2 | $0+3 \times 735 - 210 = 22584$ | | 6 | $0+4 \times 720 - 860 - 210 = 22566$ | 21 | | |
| 22682 | 4 | $0+4 \times 735 - 856 = 22673$ | | 9 | $0+4 \times 720 - 930 = 22706$ | 22 | $a_0 + 2 \times 725 + 2 \times 220 = 22646$ | 20 |
| 22748 | 2 | $0+3 \times 735 - 30 = 22764$ | | 16 | | | | |
| 22774 | 5 | $0+3 \times 735 = 22704$ | | 20 | $0+4 \times 720 - 860 = 22776$ | 2 | $b_0 + 3 \times 725 = 22768$ | 6 |
| 22928 | 2 | | $0+711 - 228 = 22911$ | 17 | $0+3 \times 720 = 22916$ | 28 | $a_0 + 3 \times 725 = 22931$ | 11 |
| 23139 | 10 | | $0+711 = 23139$ | 0 | $0+6 \times 720 - 2 \times 860 - 210 = 23146$ | 4 | $a_0 + 3 \times 725 + 220 = 23151$ | 1 |
| 23352 | 6 | | $0+711 + 212 = 23351$ | 1 | $0+6 \times 720 - 2 \times 860 = 23356$ | 6 | $a_0 + 3 \times 725 + 2 \times 220 = 23371$ | 9 |
| 23505 | 2 | $0+4 \times 735 = 23529$ | | 24 | $0+5 \times 720 - 860 = 23496$ | 25 | $b_0 + 4 \times 725 = 23493$ | 28 |
| 23589 | 2 | | $0+2 \times 711 - 228 = 23622$ | 1 | $0+7 \times 720 - 860 - 930 - 2 \times 210 = 23586$ | 10 | | |
| 23653 | 2 | | | | $0+4 \times 720 = 23636$ | 13 | $a_0 + 4 \times 725 = 23656$ | 7 |
| 23847 | 8 | | $0+2 \times 711 = 23850$ | 3 | $0+7 \times 720 - 2 \times 860 - 210 = 23866$ | 6 | $a_0 + 4 \times 725 + 220 = 23876$ | 4 |
| 24072 | 6 | | $0+2 \times 711 + 212 = 24062$ | 10 | $0+7 \times 720 - 2 \times 860 = 24076$ | 15 | $a_0 + 4 \times 725 + 2 \times 220 = 24096$ | 5 |
| 24277 | 2 | $0+5 \times 735 = 24264$ | | 13 | | | | |
| 24573 | 5 | | $0+3 \times 711 = 24561$ | 12 | $0+8 \times 720 - 2 \times 860 - 210 = 24586$ | 2 | $a_0 + 5 \times 725 + 220 = 24601$ | 13 |
| 24775 | 4 | | $0+3 \times 711 + 212 = 24773$ | 2 | $0+8 \times 720 - 2 \times 860 = 24796$ | 1 | $a_0 + 5 \times 725 + 2 \times 220 = 24821$ | 26 |
| 25011 | 2 | $0+6 \times 735 = 24999$ | | 12 | | | | |
| 25283 | 3 | | $0+4 \times 711 = 25272$ | 11 | | | | |
| 25494 | 2 | | $0+4 \times 711 + 212 = 25484$ | 10 | | | | |
| 25988 | 1 | | $0+5 \times 711 = 25983$ | 5 | | | | |
| 26199 | 1 | | $0+5 \times 711 + 212 = 26195$ | 4 | | | | |

was taken by him as indicative of one upper state only. In the overlapping region of fluorescence and absorption, two close lying common bands, named a_0 and b_0 are *sometimes* observed which, at low temperatures, show according to him an interesting relationship. He says that, "in fluorescence, the lower frequency band b_0 is always more intense than the a_0 band while in absorption the reverse is usually the case". These two bands in the case of acetate, are marked in the figure 1, according to his terminology. According to what he says, the band a_0 must be more intense in absorption than b_0 . An examination of the spectrum clearly shows that such is not the case, either in absorption or in fluorescence. As a matter of fact b_0 is by far more intense and sharper in absorption than a_0 in acetate. We examined whether his statement is correct with reference to other simple uranium salts. We tabulate below the results.

TABLE II

| Substance | Fluorescence | Absorption |
|--------------------|------------------------------|------------------------------|
| Uranyl acetate | a_0 20728 cm ⁻¹ | a_0 20756 cm ⁻¹ |
| | b_0 20583 " | b_0 20593 " |
| Uranyl chloride | a_0 | a_0 |
| | b_0 20535 " | b_0 20534 " |
| Uranyl fluoride II | a_0 20234 " | a_0 20234 " |
| | b_0 20082 " | b_0 20082 " |
| Autunite | a_0 | a_0 |
| | b_0 19848 " | b_0 19848 " |
| Uranyl nitrate | a_0 | a_0 |
| | b_0 20584 " | b_0 20591 " |

In nitrate, on which we have our own data besides those of Dieke and Duncan, a band corresponding to a_0 is not observed at all, while b_0 is very strong, in absorption. Besides, it is again the starting point for the fluorescence and is strong. In the case of uranyl chloride there is no a_0 band either in fluorescence or in absorption according to his own data. From Van Heel's data, used by Pant, the a_0 band is absent in the case of autunite. It is only in uranyl fluoride II where Pant published a spectrum of both fluorescence and absorption, we find evidence of the presence of these two bands in both and a suggestion of such an exchange of intensities. So we are inclined to consider this two-band-intensity theory, an exception rather than the rule in the case of uranyl salts. In the

fluorescence spectrum as well, the band b_0 is definitely more intense than a_0 (see figure 1(c)). In acetate, both Freymann and Pant considered that they have obtained bands corresponding to a_0 and b_0 . As a matter of fact, Pant assumed the data of Freymann. We made a close examination of this point, by comparing the data of our bands with various workers. The band b_0 (our A) was found by us to be $\nu 20589 \text{ cm}^{-1}$, 20587 cm^{-1} by Nichols and Howes and 20593 cm^{-1} by Freymann. A very good agreement can be easily observed. The average value of the absorption band b_0 is $\nu 20590 \text{ cm}^{-1}$. In fluorescence, the average value appears to be $\nu 20588 \text{ cm}^{-1}$ which is in very good agreement with the absorption value. A similar band was found at $\nu 20725 \text{ cm}^{-1}$ by various workers both in fluorescence and absorption. If we compare the average measurements in fluorescence and absorption for this band, we get $\nu 20732 \text{ cm}^{-1}$ and 20750 cm^{-1} respectively, with a deviation of at least 18 cm^{-1} between the two measurements. One is inclined to doubt whether really both bands are the same. If they are not, then the views about the intensities require reconsideration. Pant's hypothesis of two lower states, was mainly based on his idea of the a_0 and b_0 bands and their intensity variation. Our experimental evidence definitely shows that there is no such peculiarity in intensity behaviour of these bands and the strong band in absorption is also the strong band in fluorescence. Thus, apart from the additional difficulties of interpreting the origin of two low lying electronic states, the experimental facts do not appear to warrant such a hypothesis.

Figure 1(a) was reproduced from a plate on which we could record the (0,1) band with respect to $\nu 20589 \text{ cm}^{-1}$ as (0,0) definitely and possibly (0,2) also with the same path length and temperature as we used for the strong violet bands. This fact was, however, not mentioned by Freymann in his analysis. These two bands gained in intensity with higher temperatures and longer path lengths. This is a clear indication of these bands being associated with vibrational levels, of the ground state. (The usual technique for obtaining the ground state vibrations in the study of the absorption spectra of organic molecules is to obtain the spectra at higher vapour pressures and longer path lengths.)

If we adopt Freymann's (0,0) band, we do not find any interpretation for these two bands except in terms of possibly combinations without fundamentals.

For these various reasons, a detailed and fresh attempt at analysis was found to be desirable. In the actual analysis, steps were taken, on an analogy with the usual requirements in the spectra of organic molecules like substituted benzenes etc.

Our analysis.

It was found in the spectra of the substituted benzenes etc. that the (0,0) band generally corresponds to the strongest band on the long wavelength side of the spectrum for well known reasons. On this analogy, we have chosen the strong

band (A) at $\nu 20589 \text{ cm}^{-1}$ as the (0,0) band and found the shift of other bands from this. On the long wave length side of band A, we found a weak band shifted by 856 cm^{-1} which corresponds to one of the Raman frequencies (860 cm^{-1}) ascribed to the uranyl radical. A still weaker band at $\nu 18855 \text{ cm}^{-1}$ developed in longer path lengths could be interpreted as an overtone of this fundamental. These two long wavelength side bands, demonstrated in our pictures, do not find a place in earlier work. They cannot also be interpreted any other way except by the choice of A, as the (0,0) band. In fact, we are inclined to take these bands as a justification for the choice of our (0,0) band in preference to any other band (c.f. as Freymann's choice). Further, if we take this as the (0,0) band, the weak band B, obtained in fluorescence and shifted by 701 cm^{-1} from our (0,0) band, readily finds an explanation as $0+701$ corresponding to $0+735$ band in absorption (B). The difference of 30 cm^{-1} may be attributed to the weakness of the fluorescence band and a consequent uncertainty in our measurements besides any natural deviation to be expected from fluorescence to absorption data. We consider the observation of this band in fluorescence as a final justification for the choice of our (0,0).

In each of the groups B, C, D etc. the third band (shortest wave length) was found to be the most intense and successive separations of these bands from A i.e. A to B, B to C, C to D etc. are found to be of the order of 735 cm^{-1} . This obviously corresponds to a fundamental in the upper state and taking the A to B value as 735 cm^{-1} , the other bands are explained as the overtones of this fundamental. Upto D i.e. $3 \times 735 \text{ cm}^{-1}$, it is easy to follow this pattern and beyond this point, we are guided by the numerical coincidences up to $6 \times 735 \text{ cm}^{-1}$. A close examination at the point F, in particular, reveals a structure of bands quite similar to the structure of B, C, D and justifies the assignment. The agreement between the calculated and the observed values may be seen from the Table I to be quite satisfactory. Then we attempted an interpretation of the set-lite bands of B, C, D etc. The middle band was found to be at -30 cm^{-1} to the 735 band in each case and so, this was interpreted as a difference frequency between the upper state frequency 735 cm^{-1} and a ground state frequency 30 cm^{-1} . This low frequency has already been suggested as a lattice vibration by Freymann (1948). It was found quite useful to adopt this view. Similar bands in C, D, and F are given similar interpretations. The longest wave length bands in the triplets of B, C, D etc. could be interpreted as a difference frequency like $0+n \times 735 - 856 \text{ cm}^{-1}$. This interpretation finds justification from the fact that, we are definitely able to obtain the band $0-856 \text{ cm}^{-1}$.

After the above part of the analysis, we could not make much progress with the other bands notably those at Z, Y, X, M, N, etc. We again had to obtain a clue from the structure of the band pattern. The doublet set Y, X, M, N, etc. were found to have a mean separation of 212 cm^{-1} , which is very suggestive.

It was also found that the separation of the long wavelength band of the doublet from Z was about 711 cm^{-1} . Corresponding bands at Y, X, M, N etc. were found to have a mean separation of 711 cm^{-1} . The appearance of these bands is quite different from those at A, B, C, D. The bands are more diffuse and broader and are obtained distinctly only with extremely thin path-lengths. Band Z, which is extremely intense, does not find an interpretation in the analysis of Freymann, while Pant interpreted as some combination band. We felt that, if we take the band Z as starting another system, we will be able to account for its intensity and also interpret Y, X, M, N as $0+n\times 711$ and $0+n\times 711+212$. Obviously, the 711 is an upper state frequency and 212 cm^{-1} also is to be treated as such. There is another way of interpreting these doublet at Y, X etc. with Z as (0,0) as $0+n\times 930$ and $0+n\times 930-212$. In this kind of interpretation, 930 cm^{-1} corresponds to an upper state frequency, while 212 cm^{-1} corresponds to a lower state frequency. However, we are inclined to reject this possibility for the following reasons. The lower state frequency corresponding to 923 cm^{-1} is the Raman frequency 930 cm^{-1} which is definitely established to represent a non-totally symmetrical vibration. It is not reasonable to obtain a fundamental of a non-totally symmetrical vibration along with its overtones, in what appears to be an allowed kind of transition from intensity considerations. Thus, we are inclined to consider our earlier interpretation on the basis of 711 and 212 cm^{-1} as being more reasonable. 711 cm^{-1} can be taken as corresponding to 735 cm^{-1} in System I. The difference in these two upper state frequencies can be easily understood, if we associate them with two different electronic levels. There is, however, the other frequency 212 cm^{-1} which had to be assumed. The corresponding Raman frequency is 210 cm^{-1} . This means that there is practically no change in the frequency value for both upper and lower states. While normally, we expect a fall in the upper state vibrational frequency compared with the ground state frequency, it is not unusual that, there is no such change particularly with reference to the bending modes of vibration to which actually this value is attributed. It was found in the analyses of a series of substituted anisoles and toluenes from our laboratory that the CH_3 bending frequency which has about 1280 cm^{-1} occurs with practically unchanged values in both the states (Ramakrishna Rao and Suryanarayana 1955).

The choice of the Z band as the (0,0) of the second system, was further justified by the fact that we were able to identify two bands on the long wavelength side shifted by 841 cm^{-1} and $2\times 841\text{ cm}^{-1}$. This value 841 cm^{-1} may be considered as being identical with 856 cm^{-1} , the ground state frequency in System I. The band $0-2\times 841$ (System II) is actually the a_0 band of Pant [figure 1(b)]. This explanation of the a_0 band is preferred by us, instead of its association with the bands of System I. The appearance of this band is more like those of the groups Z, Y, X etc. than those of the groups A, B, C, D. One possible objection

to this interpretation can be the medium intensity with which this band occurs at the liquid air temperatures. It is generally assumed that these high frequency levels are less populated at low temperatures (exponential relationship) and so the bands are expected to be absent. However, we have to remember that this discrete absorption in the uranyl salts makes its presence felt only at such low temperatures. At high temperatures, what we get is some sort of continuous patchy absorption. It is obvious for this reason that we should not attach too much of importance to the population-frequency temperature relationship in this particular case. Further, in System I, we definitely were able to show the bands corresponding to the ground state frequencies. So, there is definitely a certain amount of population of molecules in the 856 and 2×856 vibrational levels. Only the corresponding bands are more intense in the second system than the first. This is possible because the second transition may, as a whole, have a greater intensity than the first transition.

By treating the α_0 band of Pant in this manner as the $0 - 2 \times 841$ of the second system, we can also understand why it does not occur in certain other uranyl salts, like nitrate, chloride etc. as being only due to the absence of an overtone in some cases. We also hold that this band, at $\nu 20750 \text{ cm}^{-1}$ is not necessarily the same as $\nu 20728 \text{ cm}^{-1}$ obtained in fluorescence.

A band at $\nu 20625 \text{ cm}^{-1}$ (Nichols) was not obtained by us but was found by earlier workers. It is shifted by 36 cm^{-1} to the violet of the (0,0) band of System I. If we can adopt this as the upper state frequency of the crystal lattice vibration, this, like the bending vibration, remains practically unchanged from state to state. This explains the $\nu 20823 \text{ cm}^{-1}$ band also as $0 + 36 + 212 \text{ cm}^{-1}$, the value 212 cm^{-1} being borrowed from the second system. This band was not otherwise to be explained. However, our assignment of these two bands is not definite.

For purposes of comparison, we have given in Table I, the observed and calculated values and also the deviation. The last four columns contain similar data for Freymann's and Pant's analyses. The deviations, given, were between these calculated values and their observed values. It can be seen that our analysis shows less deviation from the observed values, apart from the fact, that we are able to interpret all bands.

TABLE III

| Upper state | | Lower state | | Raman and infra-red | Assignment |
|-------------|-----------|-------------|-----------|---------------------|---------------------------------------|
| System I | System II | System I | System II | | |
| — | — | — | — | 930 | U-0 antisymmetrical |
| 735 | 711 | 856 | 841 | 860 | U-0 symmetric stretching |
| — | 212 | 210 | 228 | 220 | 0-U-0 symmetric bending |
| 36 | — | 30 | — | — | Crystal lattice vibrational frequency |

In the above Table III the probable values of the vibrational frequencies in the three electronic states are given. The non-totally symmetric frequency 930 cm^{-1} does not find a place in our analysis in any of the states, the other frequencies are observed at one stage or another with some modification of values. The totally symmetric (U-0) stretching frequency undergoes a reduction by about 12 percent from the ground state to the upper state values. The other two frequencies (0-U-0 bending and crystal lattice) practically remain unchanged in the various states.

Two systems like this can be further justified on comparison with some spectra of organic molecules. In β - and α -fluoro naphthalenes (Rao and Rao, 1955; Ramamurty and Rao, 1956) for instance, two such systems were definitely found. The system on the long wave length side, consists of sharper bands while the one on the shorter wave length side consists of diffuse bands. The two systems were distinct and separate in the substituted naphthalenes. In the present case also, the difference in the appearance of the bands of the two systems is quite clear. Only, there is an overlap of these two systems. In fact, Dieke 1949, suggested the possibility of more than one transition constituting the absorption of the uranyl salts.

We might finally suggest a tentative energy level diagram for these bands in the following figure 3. Level α represents the common ground state to which transitions take place from the two upper levels β and γ . The shift between the β and γ is 1839 cm^{-1} which corresponds to about 0.228 e.v.

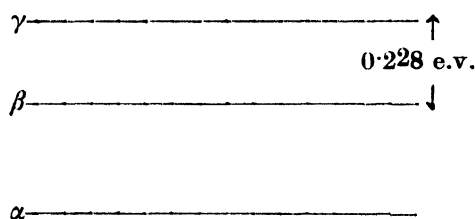


Fig. 3.

At the present stage, we do not consider it useful to discuss the exact nature of the electronic states or the exact types of transition, whether forbidden or allowed. It is our plan to carry out a systematic investigation of the absorption and fluorescence spectra of various uranyl salts, both single and double and arrive at a self consistent schemes of analyses. We may add, however, that we succeeded already, in interpreting the spectrum of uranyl nitrate on similar lines. The results will be published shortly after some confirmatory type of experimental work.

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