THE INFLUENCE OF WATER OF CRYSTALLIZATION UPON THE FLUORESCENCE AND ABSORPTION SPECTRA OF URANYL NITRATE.

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THE most striking characteristic of the fluorescence spectra of the uranyl salts is the presence of series in which the bands, when plotted on the frequency scale, are spaced at constant intervals. The frequency interval is apparently the same for the different series in the spectrum of a given salt and varies only slightly from one salt to another. The spectra observed with different uranyl salts are so similar in their general characteristics that we can scarcely doubt that the nature of these spectra is chiefly determined by the radical UO_2. Apparently the uranyl radical contains a group of electrons whose arrangement is such as to permit of vibrations that give this type of spectrum; and although UO_2 is not stable in the chemical sense and must be combined with some acid in order to form a stable compound, yet the effect of the acid radical is merely to modify the constants of this vibrating system in the UO_2 radical without changing the type of vibration. It is natural to expect that the addition of water of crystallization would produce a similar effect; and it is our intention to present in this paper the results of a study of the influence of water of crystallization upon the fluorescence and absorption spectrum in the case of uranyl nitrate.

The nitrate is particularly suited for such an investigation because of the fact that several different hydrates are formed. Crystals grown from a water solution contain six molecules of water. In an acid solution crystals are formed with three molecules of water. In both cases crystals may be obtained which are large enough to permit of observations being made with a single crystal. By methods described later small crystals containing only two molecules of water are readily obtained. It is a matter of some difficulty to push the dehydration further, but specimens have been prepared for us by Mr. D. T. Wilber which we have reason to believe are either anhydrous or formed of a mixture of the anhydrous salt and the monohydrate.

In the case of the hexahydrate wave-lengths were in most cases determined photographically. Visual observations were, however, also made,

although these could not be extended throughout the whole spectrum. The agreement between measurements made by the two methods was surprisingly good. In the case of weak bands lying near to bands of great intensity the visual observations were found to be best. The results given for the fluorescence spectra of the other hydrates and for the anhydrous salt are based upon visual observations exclusively.

For observations of the fluorescence spectrum the carbon arc was generally used as an exciting source, suitable absorbing screens being interposed to cut wave-lengths longer than about 4800 A.U. In studying absorption the continuous spectrum of the gas filled tungsten lamp was found more satisfactory, although the carbon arc was also used.

All observations were made at the temperature of liquid air.

THE HEXAHYDRATE, $UO_2(NO_3)_2 + 6H_2O$.

The hexahydrate crystallizes in the rhombic system with the axial ratio $a : b : c = .6837 : 1 : .6088$. The crystals were grown in the form of plates by using a water solution whose depth was equal to the thickness of the plate desired. Single crystals as large as 15 mm. in diameter were obtained with relatively little difficulty. All of the results here discussed are based upon observations made with single crystals. The general character of the spectrum is shown in Fig. 1.

In the great majority of cases wave-lengths were measured photographically, both in the fluorescence spectrum and in the absorption

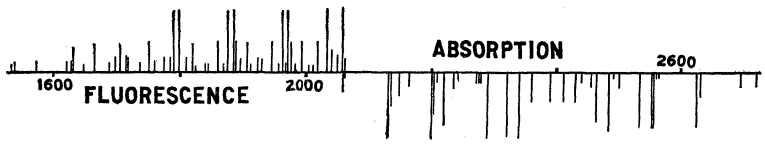

Fig. 1.

Fluorescence and absorption spectra of uranyl nitrate hexahydrate. Fluorescence bands are plotted above the line; absorption bands below. The intensity is roughly indicated by the length. The horizontal scale is one of reciprocal wave-lengths.

spectrum. In the few instances where visual observations were also made, these were found to agree remarkably well with the results obtained from photographs. In selecting the data to be used in taking a final average each negative was carefully studied and measurements that seemed for any reason doubtful were discarded. The elimination of doubtful observations was made without reference to the agreement or lack of agreement between the different measurements, and was in fact completed before the measurements of the different negatives were compared. About forty negatives were used, although the number used for any one line was rarely more than ten.

The errors of calibration of the spectrograph and spectrometer can hardly exceed 1 A.U. except perhaps in the extreme red end of the spectrum. The uncertainties due to the faintness of certain bands, to their finite width, and to photographic broadening are more difficult to estimate and undoubtedly differ greatly with the character of the band and its position in the spectrum. In the case of the sharper bands of

TABLE I.

Series in the Fluorescence Spectrum of Uranyl Nitrate Hexahydrate $[UO_2(NO_3)_2 + 6H_2O]$.

	Intensity.[1]	Reliability.[2]	$\frac{1}{\lambda}$.[3]	$\Delta\frac{1}{\lambda}$.		Intensity.	Reliability.	$\frac{1}{\lambda}$.	$\Delta\frac{1}{\lambda}$.
A	v. d.	2	F 1760.1		F	m.	1?	F 1631.3	
	v. d.	1	1846.0	85.9		d.	3	1718.4	87.1
	d.	2	1930.1	84.1		m.	4	1803.6	85.2
	m.	4	F 2018.2	88.1		m.	5	1889.6	86.0
						m.	5	1976.4	86.8
B	v. d.	3	F 1689.5			d.	4	F 2061.9	85.5
	d.	3	1775.0	85.5					
	m.	4	1861.1	86.1		m.	4	A 2061.7	
	m.	5	1947.1	86.0		m.	4	A 2148.7	87.0
	str.	5	F 2034.5	87.4		m.	4	A 2234.1	85.4
	d.	3	A 2207.3	86.4(2)		str.	3	A 2321.0	86.9
						v. d.	1	A 2491.9	85.5 × 2
C	d.	3	F 1699.0						
	d.	2	1785.1	86.1	G	d.	3	F 1810.4	
	d.	2	1869.0	83.9		d.	4	1897.3	86.9
	v. d.	1	1956.2	87.2		v. d.	2	1983.1	85.8
	m.	2	2041.5	85.3		d.	1	A 2241.6	86.2 × 3
D	v. d.	1	F 1534.9		H	v. d.	3	F 1649.7	
	d.	3	1621.0	86.1		v. d.	2	1737.4	87.7
	m.	4	1706.8	85.8		d.	1	1822.0	84.6
	str.	5	1792.5	85.7		m.	4	1906.7	84.7
	str.	5	1877.8	85.3		m.	4	1993.4	86.7
	str.	5	1963.6	85.8					
	d.	3	2050.0	86.4	I	v. d.	2	1826.0	
						v. d.	2	1911.7	85.7
E	v. d.	1	F 1540.1						
	d.	2	1629.2	89.1	J	d.	3	F 1665.5	
	m.	3	1715.0	85.8		m.	3	1751.8	86.3
	str.	5	1800.0	85.0		d.	3	1837.8	86.0
	str.	5	1886.1	86.1		m.	4	F 1923.1	85.3
	str.	5	1972.5	86.4					
	str.	5	F 2058.5	86.0		d.	4	A 2268.3	86.3 × 4
						d.	1	A 2440.2	86.0 × 2
	m.	5	A 2058.6						

[1] Estimated. Str., strong; m., medium; d., dim; v. d., very dim.

[2] The most reliable results (as indicated by the number and consistency of the individual measurements, the appearance of the negatives, etc.), are marked 5; the least reliable by 1.

[3] The unit in which $1/\lambda$ is expressed is such that for $\lambda = 5{,}000$ A.U. $1/\lambda$ is written 2000.

moderate intensity we feel that the averages that are here tabulated are reliable within 1 A.U. In other words the reciprocal wave-lengths are accurate to within about .02 per cent. For the faint or hazy bands the possible error is undoubtedly much greater.

Of the fifty-five fluorescence bands observed forty-six can be arranged in nine series as tabulated below, the frequency interval being nearly constant in each series. Two of the remaining bands have the same interval, and apparently form part of a series whose other members were too weak to detect. The seven bands that do not fall in any series arrangement are all extremely weak and since in most cases they are recorded only once their existence is subject to considerable doubt. Estimates are given in the table of the intensities of the different bands and of the reliability of the measurements. In some cases the series seem to extend into the region of absorption and in such cases the absorption bands that seem to form part of the series are also given.

The data for series B, D, E and F, which are made up of the stronger bands and those of medium intensity, are undoubtedly the most reliable. The values of the average interval between bands in these series are 86.0, 85.8, 85.9 and 86.1 respectively. In taking these averages the first band in the case of series D and E has been left out of consideration on account of its relative uncertainty. For the other series the interval, although less certain, has nearly the same value. It will be noticed that there is nothing to indicate any change in the interval as we pass from the longer to the shorter waves.

In a spectrum consisting of so many bands the occasional repetition of any given interval between bands is to be expected, even if the bands are distributed at random. It is proper to inquire, therefore, whether this interval of about 86.0 really occurs more frequently than would be expected for a random distribution. Data bearing on this point are plotted in the upper curve of Fig. 2. In this curve horizontal distances indicate the lengths of different possible intervals between bands, while ordinates give the number of times each interval occurred. The range of possible error in the location of each band is arbitrarily assumed to be 2 units. Thus for a frequency interval 32 (abscissa) the ordinate is 10. This means that ten pairs of bands were found for which the interval lay between 31 and 33.

It is evident from the chart that certain intervals occur with much greater frequency than would be expected if the bands were distributed at random, and this is most conspicuously true of the interval 86. It will be noted that the curve also shows lesser maxima for several other frequency intervals: *e. g.*, 8, 16, 70, 78 and 94. These intervals correspond

to the spacing of the bands in the successive groups which make up the spectrum.

On account of the fact that large clear crystals could be obtained the hexahydrate offered an especially favorable case for the study of the

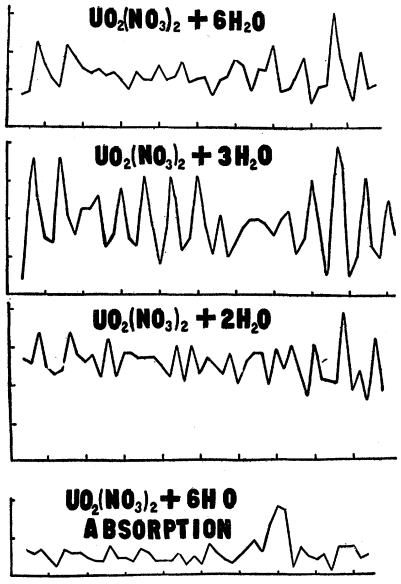

Fig. 2.

Showing the frequency of occurrence of different intervals between bands. Abscissas show the intervals (1 division = 10). Ordinates show the number of times the interval occurs (1 division = 10).

absorption spectrum. Observations were made with a number of different crystals ranging in thickness from a few tenths of a millimeter to three or four mm. The averages given in Table II. are in many cases based upon fifteen or more independent measurements. In the case of the band at 2148.7, for example, 17 measurements of wave-length were made, of which three were discarded because of the unsatisfactory character of the negatives. In the fourteen measurements used in for the average the reciprocal wave-length ranged from 2147.8 to 2 most of the values lying close to the average. In other cases th length is much more uncertain. The extremely faint band a for example, was observed on only two negatives; while the band at 2720.3 was observed only once. The reliability . . t average has been estimated in each case and is indica . . in

A study of the absorption spectrum shows that an inte

TABLE II.

Series in the Absorption Spectrum of Uranyl Nitrate Hexahydrate $[UV_2(NO_3)_2 + 6H_2O]$.

Series.	Intensity.	Reliability.	$\frac{1}{\lambda}$.	$\Delta\frac{1}{\lambda}$.	Series.	Intensity.	Reliability.	$\frac{1}{\lambda}$.	$\Delta\frac{1}{\lambda}$.
c	v. d.	2	2127.2		h	m.	5	2148.7	
	str.	4	2200.4	73.2		str.	5	2219.2	70.5
	d.	5	2272.3	71.9		str.	4	2290.2	71.0
						m.	4	2359.4	69.2
			[2053.4]			m.	4	2430.1	70.7
d′	v. d.	4	2125.0	71.6		d.	4	2500.0	69.9
	d.	2	2196.8	71.8					
	d.	4	2268.3	71.5	α	d.	5	2164.0	
	str.	3	2340.4	72.1		d.	4	2235.4	71.4
	m.	3	2412.0	71.6					
	str.	3	2484.1	72.1	β	str.	4	2321.0	
	str.	3	2555.3	71.2		m.	3	2390.0	69.0
e	str.	5	[2058.5]		γ	str.	2	2464.3	
	m.	5	2058.6			str.	4	2533.2	68.9
	str.	4	2131.2	72.6					
	m.	4	2203.8	72.6	δ	str.	4	2552.8	
	d.	4	2277.8	74.0		str.	4	2623.3	70.5
						d.	2	2695.0	71.7
f	d.	4	[2061.9]						
	m.	4	2061.7		δ'	d.	3	2559.5	
	str.	5	2134.1	72.4		m.	4	2630.5	71.0
	m.	4	2207.3	73.2					

71 between bands is of relatively frequent occurrence. (See the lower of curve Fig. 2.) In several instances definite series exist with this constant interval. The values of $1/\lambda$ for the bands forming these series are given in Table II.

The two series e and f begin with reversible bands. Thus the first band of series e, at $1/\lambda = 2058.6$, cannot be distinguished in position from the last band, $1/\lambda = 2058.5$, of the fluorescence series E, while the first band $1/\lambda = 2061.9$, of series f is coincident with the band 2061.7 of fluorescence series F. There is some indication that several other absorption series may be looked upon as associated with fluorescence series in the same way. Thus the series d′ may perhaps be associated with a very weak fluorescence series falling between D and E. Two bands of such a series were occasionally observed at 1968.0, and 2053.4 (interval 85.4). The interval between the line at 2053.4 and the first line of series d′ is 70.6, which is almost exactly the average interval for the absorption series. Again in the case of series h we might expect an absorption band to fall at 2078.7, while series H might have a fluorescence band at nearly the same point, viz., 2079.3. Neither band was observed.

But it must be remembered that the detection of reversible bands is only possible when the conditions of excitation are suitable. Any trace of fluorescence tends to mask an absorption band, and vice versa. The scarcity of bands, either of fluorescence or absorption, in the " reversal region " lying between 2060 and 2120 is perhaps due to this cause. There are other cases which suggest the same relationship between fluorescence and absorption series, although less definitely.

While there are thus strong reasons for believing that certain fluorescence series are to be looked upon as associated, in the manner indicated above, with absorption series, yet there are several series in the fluorescence spectrum for which no related absorption series have been observed; and on the other hand there are several absorption series which do not appear to be related with the observed fluorescence.

The observed intervals between bands are not so nearly constant in the case of the absorption series as in the fluorescence series. It seems to us probable that this is due to the greater uncertainty in the wave-length determinations; for on account of the lack of sharpness of the absorption bands and their greater width, as compared with the fluorescence bands, the accuracy that is attainable in determining their location is considerably less than in the fluorescence spectrum.

It will be noted also that the interval between bands is different for different series. For series e the average interval is 73.1; for series d′ it is 71.7; for series h, 70.3; while for the two pairs of lines in the ultra-violet, which have been designated as series β and γ, the interval is in one case 69.0 and in the other 68.9. This change in interval as we pass from one series to another, which is too great to be accounted for by experimental errors, appears of especial significance when it is remembered that in the fluorescence spectrum the interval is the same for all the series.

One of the most puzzling points brought out by the detailed study of the observed spectra is the fact that a considerable number of the absorption bands are spaced with the interval corresponding to the fluorescence series, and in some cases appear to form a continuation of these series. In such cases the reciprocal wave-lengths for these bands are included in Table I but are preceded by the letter A. Thus there are four absorption bands, in addition to the reversible band, which apparently belong to series F. If it is assumed that they do form a part of this series the average interval for the whole series comes out exactly the same as for the fluorescence bands alone. Series J appears to include two absorption bands, and series B, E, and G each show one band. On the whole, however, we are inclined to look upon these cases as the

result of accidental coincidences and to believe that the fluorescence series do not extend into the absorption region beyond the reversible band.

The interval of about 70, which appears to be characteristic of the absorption spectrum, is also found in the fluorescence spectrum. Thus the bands of series C are displaced from those of series E by intervals ranging from 69.0 to 70.2. A similar relation appears to exist between series J and series H, the average displacement being 70.1. Between series B and A the average shift is 70.6, between series F and H, 68.1, between series D and B, 69.1. With the exception of series I the series thus seem to be grouped in pairs, the interval between pairs being in the neighborhood of 70. It seems not unlikely that a companion series exists for I also, since faint bands were occasionally observed at 1826.0 and 1911.7 (interval 85.7) which are displaced by the intervals 71.3 and 71.4 from the corresponding bands of series I.

THE TRIHYDRATE, $UO_2(NO_3)_2 + 3H_2O$.

The trihydrate crystallizes in the triclinic system with the axial ratios $a : b : c = 1.2542 : 1 : 0.70053$.[1] The crystals were grown by evaporating the nitric acid solution in a desiccator over caustic potash and sulphuric acid or over calcium chloride. To obtain large crystal plates the bottom of a dish 6 cm. in diameter was covered with the solution to a depth of about 2 mm. and the solution was "seeded"

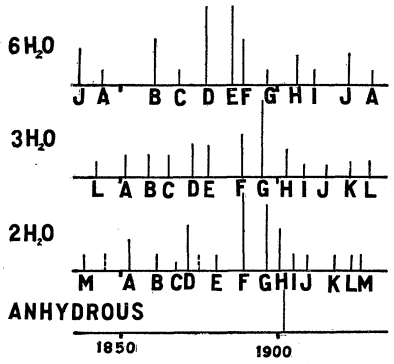

Fig. 3.

Showing one group of bands from the fluorescence spectrum of each of the salts studied. The spectrum of the hexahydrate contains seven such groups; that of the trihydrate, six; the dihydrate, five; and the anhydrous salt, three.

near the center. A cover was then placed over the solution with a small opening at the center, so that evaporation took place directly over the crystal. The trihydrate was also obtained in the form of a fine powder

[1] Wyrouboff, Sur quelques composés de l'uranium, Bull. Soc. Française Mineral, 32, 349–50, 1909.

by efflorescence of the hexahydrate crystals in dry air. Although most of the observations recorded below were made with single crystals, a few measurements were made, with concordant results, on the powder. In the fluorescence spectrum visual observations only were made. In the absorption spectrum the measurements were in most cases photographic.

The fluorescence spectrum of the trihydrate was found to consist of 63 bands, of which 55 fell into 12 constant interval series of from three to six bands each. The intervals for the different series ranged from 86.5 to 87.5, the average being 86.8. The reciprocal wave-lengths are given in Table III. The numbers in brackets refer to absorption bands which seem to fall into the fluorescence series. The relative intensities of the bands are shown roughly in Fig. 3 where a typical group, *i. e.*, one band from each series,—has been plotted for each of the salts studied.

TABLE III.

Series in the Fluorescence Spectrum of Uranyl Nitrate Trihydrate, $UO_2(NO_3)_2 + 3H_2O$.

A. 1677.0, 1765.0, 1851.5, 1938.8, 2025.0, (2112.7, 2200.2)
B. 1686.1, 1772.0, 1858.7, 1945.7, 2033.2, (2120.7)
C. 1778.7, 1865.1, 1952.9, 2041.1, (2041.1)
D. 1699.8, 1785.9, 1873.0, 1959.1, 2046.8, (2134.0, 2220.6, 2307.9)
E. 1704.2, 1791.8, 1877.4, 1965.3, 2051.0
F. 1629.2, 1715.2, 1802.1, 1889.0, 1976.4, 20643.?
G. 1637.2, 1722.8, 1808.7, 1895.3, 1982.3, 2070.7
H. 1643.9, 1729.2, 1816.1, 1903.0, 1989.9, 2076.3, (2076.5, 2251.2)
I. 1821.3, 1908.9, 1995.9, (2083.8)
J. 1741.8, 1828.2, 1915.9, 2002.1, (2089.7)
K. 1748.6, 1835.3, 1923.3, 2009.8
L. 1667.2, 1755.0, 1842.4, 1930.1, 2017.4, (2103.5, 2189.2, 2277.9)

The second curve of Fig. 2, which shows the frequency of occurrence of the different possible intervals between the bands of the fluorescence spectrum, indicates a remarkably regular grouping of the bands. Besides the principal interval 87.0 which is characteristic of the series in this spectrum, a number of other intervals are almost equally prominent, *e. g.*, 7, 14, 30, 36, 43.5, 50, 80, 94. In the case of each of these intervals the frequency of occurrence is far above the average. These intervals, of course, correspond to the spacing of the bands in the groups. Thus the interval 43.5, which is just half the principal interval 87.0, occurs twice in each group, the bands of series K lying half way between the bands of series F and the bands of series L half way between those of series G. In each case the two series might be combined to form a single series with half the interval. Since, however, the bands of the combined series would be alternately strong and weak it does not appear that such a combination is justified.

In the absorption spectrum of the trihydrate 48 bands were observed, several of which, however, were so faint and indistinct as to make their existence doubtful. As in the case of the hexahydrate an interval between bands of a little more than 70 is of frequent occurrence, and 37 of the bands (including all that are strong and well defined) can be arranged in 9 constant interval series. The interval does not appear to be the same for all of these series, however. In one case the interval is as high as 73.8, while in another case its value is 71.0. For most of the series the interval lies near 72.0.

In many instances the absorption series start with reversed fluorescence bands. Reversals are especially sharp and definite in the case of the final bands of series C, G and H and L ($1/\lambda$ = 2041.1, 2070.7, 2076.3, 2104.9). In other cases the absorption series begins at a point where a fluorescence band might be expected, but where none was actually observed. Thus we should expect the final bands of series I, J and K to lie at 2082.7, 2090.0 and 2096.6 respectively. These bands were not observed, probably because of the fact that the three series in question are made up of very faint lines. But the first bands of the absorption series i, j and k, fall at 2083.8, 2089.7 and 2095.6 and it would seem, therefore, that they might properly be looked upon as resulting from the reversal of the final bands of the corresponding fluorescence series, even though these bands escaped observation.

The reciprocal wave-lengths for the principal absorption series are given below. Each series is lettered in such a way as to indicate the

TABLE IV.

Series in the Absorption Spectrum of Uranyl Nitrate Trihydrate, $UO_2(NO_3) + 3H_2O$.

b	B = 2033.2	b = (2033.2), 2107.0, 2180.8
c	C = 2041.1	c = 2041.1, 2112.7, 2186.7
c′	C′ = ?	c′ = 2043.3, 2116.0, 2189.7, 2261.0
f′	F′ = 2058.5	f′ = 2057.6, 2129.0, 2200.2, 2271.7
g	G = 2070.7	g = 2071.7, 2142.7, 2213.2, 2285.7, 2357.9
h	H = 2076.3	h = 2076.5, 2148.6, 2220.6, 2368.0
i	I = (2082.7)	i = 2083.8, 2154.5 2226.9, 2297.8, 2368.0
j	J = (2090.0)	j = 2089.7, 2162.0, 2235.4, 2307.9
k	K = (2096.6)	k = 2095.6, 2166.7
l′	L′ = ?	l′ = 2103.0, 2173.4, 2245.7, 2317.5

fluorescence series with which it appears to be related: *e. g.*, the first band of series *c* is the reversal of the last band of series *C*. In each case also the reciprocal wave-length is given for the last band of the fluorescence series. The numbers in brackets indicate bands that were not observed but would be expected to occur with the indicated value of $1/\lambda$.

It is to be observed that no absorption series were found which corresponded to the fluorescence series A, D, E and L. On the other hand no fluorescence series were observed to correspond with the absorption series c′ and l′.

The Dihydrate, $UO_2(NO_3)_2 + 2H_2O$.

Although the dihydrate has been made by several observers the crystalline form does not appear to have been studied. The crystals used in this investigation were in most cases made by heating a tube containing the crystallized trihydrate to a temperature somewhat above 100° C. and passing through it a current of air which had been run through a mixture of sulphuric acid and nitric acid and over phosphorous pentoxide. The melted trihydrate slowly evaporated and recrystallized as dihydrate without losing nitric acid. The tube was then sealed up to prevent the entrance of moisture. The dihydrate was also prepared synthetically by treating dry H_2UO_4 with the "monohydrate" nitric acid, the two being sealed in a glass tube and allowed to react. The crystals obtained were in each case small so that the observations were made on a mass of crystals having no systematic arrangement of the axes.

Seventy-four bands were observed in the fluorescence spectrum, sixty-one of which fell into twelve constant interval series of from four to six bands each. The interval ranged from 87.6 in series F to 88.3 in series A, but in most cases lay near the average of all, viz., 88.1.[1] The values of $1/\lambda$ are given in Table V., and a typical group, consisting of one band from each series, is shown in Fig. 3. Many of the bands that do not fall into these twelve series nevertheless seem to belong to similar series of which only two or three bands could be detected. Two of these suspected series have been included in Fig. 3 where they are indicated by dotted lines.

Table V.

Series in the Fluorescence Spectrum of Uranyl Nitrate Dihydrate, $UO_2(NO_3)_2 + 2H_2O$.

A.	1676.7,	1765.9,	1853.0,	1942.7,	2030.7
B.	1684.9,	1773.7,	1861.6,	1951.0,	2037.9
C.	1780.6,	1867.8			
D.	1609.0,	1695.5,	1783.5,	1871.8,	1959.7, 2047.4
E.	1618.9,	1705.9,	1794.4,	1880.3,	1967.5
F.	1625.3,	1714.3,	1801.5,	1889.5,	1977.1, 2063.1
G.	1632.7,	1721.2,	1808.5,	1896.8,	1985.2, 2072.5, (2072.7)
H.	1637.7,	1725.3,	1814.6,	1900.8,	1989.7, 2077.3, (2078.2)
I.	1641.5,	1729.8,		1905.1,	1993.8
J.	1645.3,	1734.6,	1821.2,	1909.0,	1998.4
K.	1830.5,	1918.3			
L.	1658.4,	1745.5,	1834.9,	1923.8,	2009.3, (2095.9)
M.	1751.0,	1838.2,	1926.8,	2015.5,	(2102.7, 2191.3, 2278.0)

[1] For series C, which contained two bands only, the interval was 87.2.

The absorption bands were located by observing the spectrum of light from a continuous source after diffuse reflection from a mass of small crystals. Although the bands observed in this way are surprisingly sharp the method is not so satisfactory as that in which the light is analyzed after direct transmission through a single crystal. It is doubtful whether the reflection method gives as great accuracy in the location of the bands, and many of the weaker bands, which would have been easily detected if large crystals had been available, were probably not observed at all. For this reason, perhaps, the absorption spectrum of the dihydrate shows only four well defined series. The reciprocal wavelengths for these series are given in Table IV. The interval between bands is 70.0 for series m, 70.4 for series j, and 71.3 for series g and h. In each case the first band in the absorption series occupies nearly the same position as the last band in one of the fluorescence series.

TABLE VI.

Series in the Absorption Spectrum of Uranyl Nitrate Dihydrate, $UO_2(NO_3)_2 + 2H_2O$.

G = 2072.4	g = 2072.7, 2144.7, 2215.3
H = 2077.3	h = 2078.2, 2149.4, 2218.9, 2290.4, 2362.9
J = (2085.7)	j = (2086.1), 2156.6, 2227.2, 2297.3
M = (2103.6)	m = 2102.7, 2172.7, 2242.7

THE ANHYDROUS NITRATE.

Specimens of uranyl nitrate that were in all likelihood anhydrous, and which certainly contained less water than the dihydrate, were prepared by allowing nitric anhydride, N_2O_5, to react with uranic oxide. The nitric anhydride was distilled from a mixture of nitric acid and phosphorous pentoxide, while the uranic oxide was prepared by heating uranic acid, H_2UO_4. In preparing the oxide the heating was not continued so long as to completely drive off the water from the uranic acid, since when this was done no reaction occurred between the oxide and the nitric anhydride.

At temperatures above 30° C. the N_2O_5 reacts with the mixture of UO_3 and H_2UO_4 to form uranyl nitrate, presumably anhydrous, and a considerable amount of HNO_3. To free the specimen from acid the tube containing it was placed in a freezing mixture until the N_2O_5 was frozen, when the HNO_3, which still remained a liquid, was poured off. This process was repeated several times. While the amount of water remaining after this treatment must have been extremely small, we cannot feel certain that all traces were removed, and it is possible therefore that the nitrate formed may have consisted in part of the monohydrate. No fluorescence bands belonging to the other hydrates could be observed.

The method of preparation was varied by changing the temperature at which the reaction was allowed to occur, and by heating the salt, after it had been formed, to different temperatures and for different periods.

The fluorescence spectra of the different preparations differed widely. In one case, the spectrum was found to consist of three narrow bands only. But in all other cases bands were observed which remained broad (about 100 A.U.) even at the temperature of liquid air. These bands were spaced with a constant frequency interval of approximately 88–89. It seems probable that these broad bands were due to the solution of the anhydrous salt in nitric acid. To test this point a specimen was prepared under conditions which made certain the presence of a considerable excess of nitric acid. The fluorescence spectrum contained two series of broad bands, the central band of the stronger series lying at $1/\lambda = 1939.0$ and that of a weaker series at $1/\lambda = 1920.0$. The specimen was then gently heated and the nitric acid driven off was condensed in a connecting tube. After this process had continued for a short time, several series of narrow bands or lines appeared in the fluorescence spectrum (at $-186°$ C.). As this procedure was repeated the line spectrum became more prominent and the broad bands fainter. In one instance the specimen was heated nearly to decomposition—in fact part of the salt was undoubtedly decomposed—and in this case the very faint fluorescence spectrum consisted of three narrow bands only. The same three bands were observed in the case of most of the specimens that were prepared in the attempt to remove the water of crystallization, although in other cases they were accompanied by other lines or broad bands. It seems probable that these three bands constitute the brightest part of the fluorescence spectrum of the anhydrous salt, and that the additional lines and bands that were observed in some specimens are due to traces of the monohydrate or to a solution of the nitrate in HNO_3. The three bands formed a series with the interval 88.5, the central band lying at $1/\lambda = 1902.0$.

SUMMARY AND CONCLUSIONS.

1. In the case of each of the nitrates the fluorescence spectrum is made up of series in which the intervals between bands are constant and the same for all of the series. The interval increases slightly, but unmistakably, as the amount of water of crystallization decreases. For the hexahydrate the interval is 86.0; for the trihydrate 86.8; for the dihydrate 88.1; and for the anhydrous salt 88.5.

2. Numerous constant interval series occur in the absorption spectrum, the interval being approximately 71. But the interval does not appear

to be the same for different series even when these occur in the spectrum of the same salt. No systematic variation with the amount of water of crystallization could be detected.

3. Nearly all of the series in the absorption spectrum have their origin in the "reversing region," the first member of the absorption series being in coincidence with the last member of a fluorescence series and constituting a "reversible" band.

4. There is some slight resemblance between the different hydrates as regards the grouping of the bands (see Fig. 2). In each case, for example, a certain short interval appears with a frequency considerably above the average. In the case of the hexahydrate and the dihydrate this interval is about 8; in the case of the trihydrate is almost exactly 7. The interval 14, in the case of the trihydrate, and 16, in the case of the other two salts, is also of unusually frequent occurrence. It will be interesting to determine whether this peculiarity in the distribution of intervals is characteristic of all uranyl salts.

5. It is clear from inspection of Fig. 3, in which a characteristic group of bands is shown for each of the hydrates studied, that the different spectra are not in the least similar in their general appearance. It might at first appear that the three hydrates have one series in common, viz., that designated as series F. But while the central band of this series does occupy practically the same position in each of the three spectra, the fact that the interval between bands is different for the different salts causes the bands to fall more and more out of step as we proceed in either direction from the center of the spectrum.

On the whole the spectra of the different hydrates differ from one another fully as much as do the spectra of two different uranyl salts. This result is surprising, since it is customary to think of water of crystallization as rather loosely attached and therefore incapable of exerting a great influence upon properties which depend upon the internal structure of the molecule. In the uranyl salts it appears that we must look upon the connection as more intimate than has generally been supposed. The results also tend to confirm the view that fluorescence spectra are due to vibrations which occur in the outer parts of the molecule and which are therefore readily modified by outside sources of disturbance.

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