802. *Infrared Spectra of Uranyl Nitrate Hydrates and Rubidium Uranyl Nitrate.*

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The infrared spectra of uranyl nitrate di-, tri-, and hexa-hydrate have been examined from 3700 to 700 cm.$^{-1}$, with nitrogen of normal isotopic composition and enriched in ^{15}N, and most of the bands are assigned.

The spectrum of uranyl nitrate hexahydrate is in most respects that of a typical ionic nitrate.

The spectra of uranyl nitrate di- and tri-hydrate are similar to the spectrum of rubidium uranyl nitrate, and all three are closely related to the fluorescence spectrum of cæsium uranyl nitrate, studied by Dieke and Duncan. These spectra are all characteristic of compounds having co-ordinated nitrato-groups, and structures are suggested for the molecules in crystals of the di- and the tri-hydrate which account for the observed splitting of many of the bands.

There have been several investigations of the infrared spectra of the hydrates of uranyl nitrate,[1-5] but there has been no detailed assignment of the bands. The infrared spectrum of rubidium uranyl nitrate has not hitherto been reported.

Sevchenko and Stepanov [2] examined the spectrum of the hexahydrate and, without reference to the frequencies expected to arise from the nitrate ion, assigned all the peaks in the region 870—2000 cm.$^{-1}$ to combinations or overtones of the three fundamental frequencies of the uranyl ion. They also reported the synthesis of uranyl nitrate tri-, di-, and mono-hydrate and the anhydrous compound and gave their spectra, observing that the band at 1390 cm.$^{-1}$ occurs strongly only in the hexahydrate. Although Sevchenko and Stepanov stated that the compositions of the hydrates had been established by analysis, the preparations were not described and the existence of a monohydrate and an anhydrous phase in this system is not generally recognised.[6] Burger and Moore [4] tabulated the frequencies in the infrared spectrum of uranyl nitrate dihydrate, both for the solid state and for solutions in organic solvents: they assigned the frequencies to vibrations of uranyl and nitrate ions, but without specifying the vibrations. Tridot [5] examined the spectra of the di-, tri-, and hexa-hydrate suspended in carbon tetrachloride and found them to vary markedly with the state of hydration.

Previous work on the fluorescence,[7,8,9] infrared,[1,2,10,11], and Raman [10,12,13,14] spectra of uranyl compounds, both in the solid state and in solution, has established that the uranyl ion has three fundamental vibration frequencies: A (860 cm.$^{-1}$, symmetrical stretching), B (930 cm.$^{-1}$, antisymmetric stretching), and C (210 cm.$^{-1}$, bending). The only frequency normally observed in the infrared spectrum is B, since A is forbidden for a linear ion and C is outside the usual spectral range. However, frequency A is sometimes observed weakly in the infrared spectrum and the reasons for this have been discussed by Crandall [13] and by Sutton.[14]

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[1] Lecomte and Freymann, *Bull. Soc. chim. France*, 1941, **8**, 622.

[2] Sevchenko and Stepanov, *Zhur. eksp. teor. Fiz.*, 1949, **19**, 1113 (A.E.R.E. Translation No. 11/3/5/80).

[3] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 309.

[4] Burger and Moore, U.S.A.E.C. document HW-18260 (1950).

[5] Tridot, *Ann. Chim. (France)*, 1955, **10**, 225.

[6] Katz and Seaborg, "The Chemistry of the Actinide Elements," Methuen, London, 1957, p. 193.

[7] Nichols and Howes, "Fluorescence of the Uranyl Salts," Carnegie Inst. Wash. publ. no. 298 (1919).

[8] Freymann, *J. Phys. Radium*, 1948, **9**, 158.

[9] Dieke and Duncan, "Spectroscopic Properties of Uranium Compounds," McGraw-Hill, New York, 1949, pp. 36 *et seq.*

[10] Conn and Wu, *Trans. Faraday Soc.*, 1938, **34**, 1483.

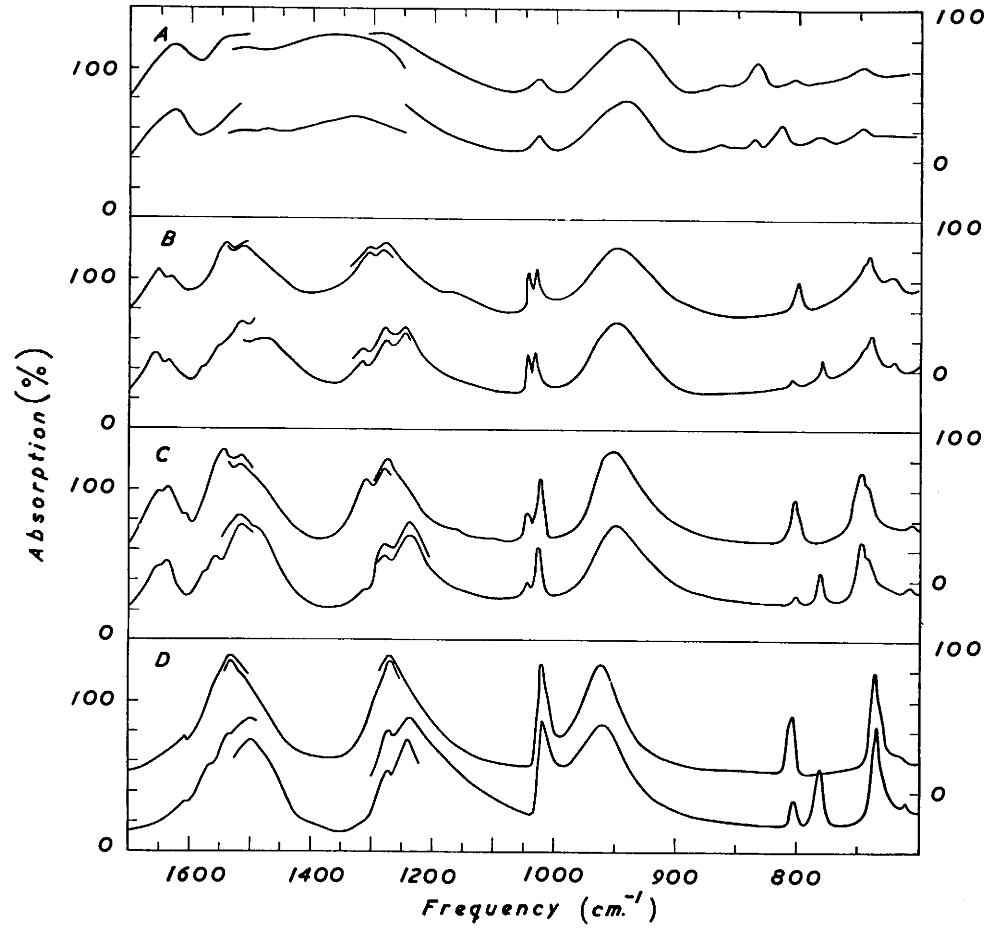
[11] Jones, *J. Chem. Phys.*, 1955, **23**, 2105.

[12] Satyanarayana, *Proc. Indian Acad. Sci.*, 1942, **15**, *A*, 414.

[13] Crandall, *J. Chem. Phys.*, 1949, **17**, 602.

[14] Sutton, A.E.R.E. C/R 769 (1951); *Nature*, 1952, **169**, 235.

The fluorescence and visible absorption spectra of rubidium and cæsium uranyl nitrate were studied in great detail by workers for the American Atomic Energy Project,[9] and the hydrates of uranyl nitrate were studied to a smaller extent. The fine structures of these spectra are closely related to the infrared spectra, but the latter were not studied by these workers.



A, $UO_2(NO_3)_2,6H_2O$; *B*, $UO_2(NO_3)_2,3H_2O$; *C*, $UO_2(NO_3)_2,2H_2O$; *D*, $RbUO_2(NO_3)_3$.

Upper curves (*ordinate scales at right-hand side*) *refer to compounds of normal isotopic composition*; *lower curves* (*ordinate scales at left-hand side*) *refer to compounds enriched in* ^{15}N. *Regions* 1200—1500 *cm.*$^{-1}$ *are for hexachlorobutadiene suspensions, other regions for Nujol suspensions.*

The only crystallographic work on these compounds has been by Pauling and Dickinson[15] who located the uranium atoms in the unit cell of uranyl nitrate hexahydrate, and by Hoard and Stroupe[16] who obtained a fairly detailed picture of the structure of rubidium uranyl nitrate.

Recent work[17] on the infrared spectra of a series of nitratocobaltammines has enabled the vibration frequencies of the co-ordinated nitrato-group to be assigned and to be distinguished from those of the nitrate ion; with these results as a guide we have re-examined the uranyl nitrate spectra.

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[15] Pauling and Dickinson, *J. Amer. Chem. Soc.*, 1924, **46**, 1615.

[16] Hoard and Stroupe, ref. 9, pp. 13 *et seq.*

[17] Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222.

EXPERIMENTAL

Materials.—Uranyl nitrate hexahydrate (" AnalaR ") was recrystallised from water and analysed by ignition to U_3O_8 at 750—800° [Found: U, 47·32, 47·26. Calc. for $UO_2(NO_3)_2,6H_2O$: U, 47·42%].

Uranyl nitrate trihydrate was prepared [18] by storing the powdered hexahydrate over sulphuric acid (*d* 1·54) *in vacuo* for 4 weeks; after 2 weeks the acid was renewed and the sample ground and replaced [Found: U, 53·24, 53·30. Calc. for $UO_2(NO_3)_2,3H_2O$: U, 53·12%]. The trihydrate was also prepared [19] in the form of large crystals by evaporating a solution of the hexahydrate in nitric acid (*d* 1·4) over solid potassium hydroxide.

Uranyl nitrate dihydrate was prepared similarly to the trihydrate (first method), but by using concentrated sulphuric acid (*d* 1·84) [Found: U, 55·41, 55·48. Calc. for $UO_2(NO_3)_2,2H_2O$: U, 55·35%]. Attempts to crystallise the dihydrate [19] from a solution of anhydrous uranium trioxide in fuming nitric acid (*d* 1·5) were unsuccessful: microscopic examination showed the crystals to be of the trihydrate.

Rubidium uranyl nitrate was prepared by dissolving rubidium nitrate (1·0 g.) and uranyl nitrate hexahydrate (3·4 g.) in separate portions of concentrated nitric acid (2 ml. and 3·5 ml. respectively) and mixing the warm solutions. Crystallisation started almost immediately and the crystals were filtered off from the warm solution. The product was dried in a vacuum-desiccator over sodium hydroxide (yield 2·5 g.) and analysed by precipitation as ammonium diuranate and ignition to U_3O_8 [Found: U, 44·53, 44·18. Calc. for $RbUO_2(NO_3)_3$: U, 43·95%].

The same compounds, enriched in ^{15}N, were prepared by similar methods from a sample of enriched nitric acid. They were not analysed, but the similarities of their spectra to those of the isotopically normal compounds, together with their methods of preparation, establish their identities. The isotopic composition of the nitric acid was not measured directly: instead, the rubidium uranyl nitrate prepared from it was decomposed thermally and the resulting oxides of nitrogen were reduced to nitrogen by iron powder. Mass-spectrographic analysis of this nitrogen showed it to contain 81·9 atoms % of ^{15}N.

Spectra.—A Grubb–Parsons double-beam infrared spectrometer was used, equipped with an S3A monochromator and a sodium chloride prism. The samples were examined as suspensions in Nujol and, for the 1200—1500 cm.$^{-1}$ region, as suspensions in hexachlorobutadiene. The cell windows were of sodium chloride coated with polystyrene: use of coated windows has been found to be essential for work on nitrates,[17, 20] since some compounds with co-ordinated nitrato-groups react with sodium chloride windows and the products give the spectrum of the nitrate ion. The reaction with uncoated windows was observed in preliminary work with uranyl nitrate tri- and hexa-hydrate, but not with the dihydrate or rubidium uranyl nitrate. The spectrum of rubidium uranyl nitrate from 700 to 400 cm.$^{-1}$ was recorded by using a Hilger double-beam spectrophotometer, model H 800, equipped with a cæsium bromide prism.

RESULTS AND DISCUSSION

The spectra of rubidium uranyl nitrate and uranyl nitrate di- and tri-hydrate are closely related and will be discussed together. The spectrum of uranyl nitrate hexahydrate is in most respects that of an ionic nitrate. They are illustrated in the Figure.

In all the spectra the frequencies of the *B* vibration of the uranyl ion (antisymmetric stretching) are close to those reported by others,[1-5, 8-11] and the *A* vibration (symmetric stretching), forbidden in the infrared for the free ion, was observed only in the spectrum of uranyl nitrate hexahydrate.

Conventions for numbering the vibrations of the nitrate ion [21] differ from those used for the nitrato-group (*e.g.*, in nitric acid,[22, 23] methyl nitrate,[24] and nitrato-co-ordination complexes [17]). To avoid confusion, since the convention for the nitrate ion is here

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[18] Katzin, Simon, and Ferraro, *J. Amer. Chem. Soc.*, 1952, **74**, 1191.

[19] Ref. 7, p. 208.

[20] Gatehouse, *Chem. and Ind.*, 1957, 1351.

[21] Herzberg, " Infra-red and Raman Spectra of Complex Molecules," Van Nostrand, New York, 1945, p. 179.

[22] Redlich and Nielsen, *J. Amer. Chem. Soc.*, 1943, **65**, 654.

[23] Ingold and Millen, *J.*, 1950, 2612; Cohn, Ingold, and Poole, *J.*, 1952, 4272.

[24] Brand and Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.

employed to describe the spectrum of uranyl nitrate hexahydrate, whereas that for the nitrato-group is used for all the other spectra, the relations between these two sets of conventions are shown in Table 1. The symmetry types of the vibrations are given in parentheses; their approximate forms have been illustrated by, *inter al.*, Redlich and Nielsen [22] and by Cohn, Ingold, and Poole.[23]

TABLE 1.

NO_3^-	ν_1 (A_1') NO stretch.	ν_2 (A_2'') Out of plane	ν_3 (E') NO_2 stretch.		ν_4 (E') NO_2 bend.	
O_2NO	ν_2 (A_1) NO stretch.	ν_6 (B_2) Out of plane	ν_1 (A_1) NO_2 stretch. symmetric	ν_4 (B_1) NO_2 stretch. antisymmetric	ν_3 (A_1) NO_2 bend. symmetric	ν_5 (B_1) NO_2 bend. antisymmetric

The fundamentals in the infrared spectra of rubidium uranyl nitrate and of uranyl nitrate di- and tri-hydrate are given in Table 2, together with the frequencies in the fluorescence spectrum of cæsium uranyl nitrate which Dieke and Duncan recognised, from their nitrogen-isotope shifts, as arising from vibrations of the nitrate ion but could not assign in detail.

Nitric acid and methyl nitrate have bands in the Raman spectrum at 680 and 610 cm.$^{-1}$, and 664 and 578 cm.$^{-1}$ respectively; but whereas Ingold *et al.*[23] assigned the nitric acid bands to ν_3 and ν_5 respectively, Brand and Cawthon [24] gave the reverse assignment for the bands in methyl nitrate. In the infrared spectrum of rubidium uranyl nitrate we observed no bands between 700 and 400 cm.$^{-1}$, but in this spectrum and in the spectra of uranyl nitrate di- and tri-hydrate a strong and a weak band appeared in the region 750—700 cm.$^{-1}$. These two bands are assigned to ν_3 and ν_5, but we have no criteria for distinguishing between these two vibrations and our assignment of the higher-frequency band to ν_3 is arbitrary.

In all of these spectra there are pairs of bands at *ca.* 1300 and 1500 cm.$^{-1}$ (ν_1 and ν_4 respectively) which are characteristic of the co-ordinated nitrato-group.[17] They are derived from the degenerate vibration ν_3 of the nitrate ion which is split when co-ordination changes the symmetry of the ion from D_{3h} to C_{2v}. In the spectra of uranyl nitrate di- and tri-hydrate vibrations ν_1, ν_2, ν_3, and ν_4 are split and ν_5 is very weak, whereas the out-of-plane vibration ν_6 is not split. Closely analogous splittings are found in the fluorescence spectrum of cæsium uranyl nitrate, but in the infrared spectrum of rubidium uranyl nitrate all six bands are single.

The infrared spectra are well accounted for if it is assumed that uranyl nitrate di- and tri-hydrate have structures analogous to that of rubidium uranyl nitrate [16] (I), the exact assumptions being (*a*) that each uranyl ion is surrounded by an equatorial ring of six oxygen atoms, which may or may not lie in a plane, and (*b*) that in the di- and the tri-hydrate all water molecules are directly co-ordinated with uranium. These assumptions necessarily imply that nitrato-groups are not shared between uranium atoms and it is therefore reasonable to discuss the nitrate-group vibrations in terms of the local symmetry of the molecule rather than in terms of the symmetry of the crystallographic unit-cell. The assumptions allow of only two possible structures for the molecule of the di-hydrate, (II) and (III), and two for the trihydrate, (IV) and (V).

In structures (I)—(V) the rings of six oxygen atoms are tightly packed and the planar vibrations of the nitrato-groups will be closely coupled; the in-phase and out-of-phase vibrations will have slightly different frequencies and thus each of the five planar modes will be split.

For the dihydrate, (II) alone would account for the splitting of the planar modes in the infrared spectrum. Although in structure (III) these vibrations would be split, only one of each of the pairs of vibrations would be infrared active.

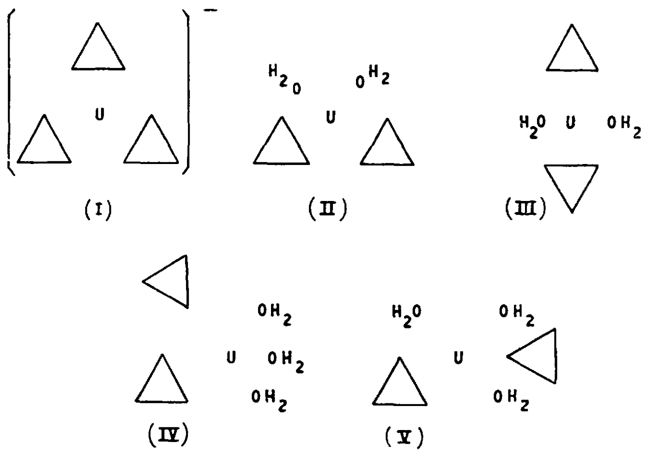
For the trihydrate, either (IV) or (V) would account for the observed splittings, but (IV) is preferred since the separation of the doublets is similar in the di- and the tri-hydrate and this implies a similar degree of coupling.

TABLE 2. *Fundamentals.*

	$RbUO_2(NO_3)_3$		$CsUO_2(NO_3)_3$ *		$UO_2(NO_3)_2,2H_2O$		$UO_2(NO_3)_2,3H_2O$	
Assignment	^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N
ν_5			708	708	706	707	720	721
	711 sh	711	713	712				
ν_3	736	736	739	738	743 sh	741 sh	743	740
			749	748	748	748	747 sh	746 sh
ν_6	803	782	805	784	801	781	800	779
B	960	960	956	956	951	951	950	951
ν_2	1023	1019	1021	1020	1026	1025	1029	1033
			1025	1024	1044	1045	1043	1046
ν_1	1276	1244	1277	split	1280	1241	1284	1246
					1311	1280	1308	1279
ν_4			1504	1471	1515	1488 sh	1517	1471
	1536	1499	1519	1480	1547	1519	1545	1515
ν_2 (H_2O)					1637	1637	1631	1634
					1650	1650	1656	1658
H_2O					3270	—	3240	—
					3360		3420	
					3560		3630	
					3690 sh		3670 sh	

* Values taken from Dieke and Duncan's fluorescence spectrum. — Not studied.

For rubidium uranyl nitrate all the planar vibrational modes should be split, but only one vibration of each pair should be infrared active. This agrees exactly with the observations.



Nitrate ions are denoted by triangles. Uranyl oxygen atoms are out of the plane of the paper, vertically above and below the uranium atoms.

Neither in the fluorescence spectrum of cæsium uranyl nitrate nor in the infrared spectra of rubidium uranyl nitrate, and uranyl nitrate di- and tri-hydrate is the out-of-plane vibration ν_6 split. This is reasonable since in vibrations of the nitrato-groups parallel to the uranyl axis there can be little interaction between neighbouring groups such as occurs in, *e.g.*, potassium nitrate.[25]

The ν_2 vibration of the water molecule is split in the spectra of uranyl nitrate di- and tri-hydrate, owing no doubt to interactions between neighbouring molecules. The bands of the water molecules in the 3000 cm.$^{-1}$ region were observed only at low dispersion and are not assigned.

Many overtones and combinations were observed in these spectra; their frequencies and probable assignments are given in Table 3. The assignments for those which showed nitrogen-isotope shifts are mostly unambiguous, but the assignments of the others are only tentative. Most of the possible combinations of two of the five planar modes of the

[25] Decius, *J. Chem. Phys.*, 1954, **22**, 1941; 1955, **23**, 1290.

nitrato-group were observed, but few involving the out-of-plane vibration. In uranyl nitrate trihydrate the two lower and the two higher frequency components of ν_2 and ν_3 both combine, but in no other case does a split fundamental yield two combination frequencies.

The infrared spectrum of uranyl nitrate hexahydrate differs considerably from the spectra discussed above: the fundamentals are given in Table 4. The hexahydrate exhibits a broad, intense band at 1366 cm.$^{-1}$, characteristic of the nitrate ion (ν_3). The nitrate ion " breathing " vibration ν_1, which is forbidden in the infrared for an isolated ion, appears here with medium intensity, presumably owing to asymmetry in the crystal environment. Similar behaviour is shown by the nitrate ion in some co-ordination compounds.[17]

The out-of-plane vibration ν_2 appears to be split into two components, separated by 32 cm.$^{-1}$, which have similar nitrogen-isotope shifts. This may be caused by association of nitrate ions in close pairs, one above the other, the two frequencies resulting from the in-phase and the out-of-phase vibration of these pairs. For an isolated pair the coupled out-of-phase vibrations would be infrared inactive, but this would not be so in the crystal if the surroundings vertically above and below each pair were different. In potassium nitrate, where nearest-neighbour nitrate ions are stacked vertically above each other in an aragonite-type lattice, this vibration is split,[25] although to a smaller extent than is that in uranyl nitrate hexahydrate. An alternative explanation would be that ν_2 is strongly coupled to a lattice vibration at 32 cm.$^{-1}$.

TABLE 3. *Overtones and combinations.*

	$RbUO_2(NO_3)_3$				$UO_2(NO_3)_2,2H_2O$				$UO_2(NO_3)_2,3H_2O$			
Assignment	^{14}N obs.	^{14}N calc.	^{15}N obs.	^{15}N calc.	^{14}N obs.	^{14}N calc.	^{15}N obs.	^{15}N calc.	^{14}N obs.	^{14}N calc.	^{15}N obs.	^{15}N calc.
$2\nu_5$	1429	1422	1424	1422								
$2\nu_3$	1473	1472	1466	1472			1488	1486				
$2\nu_6$	1608	1606	1570	1564	1608	1602	1558	1562			1553	1558
$\nu_2 + \nu_5$	1727	1734	1733	1730	1733	1732	1733	1732	1739	1749	1739	1754
$\nu_2 + \nu_3$	1761	1759	1764	1755	1783	1787	1783	1786	1779	1772	1770	1773
$\nu_2 + \nu_3$									1795	1790	1799	1792
$A + B$	1845	1848	1845	1848	1828	1831 *	1832	1831 *	1828	1824 §	1835	1825 §
$2B$					1898	1902	1898	1902				
?									1934		1942	
$\nu_1 + \nu_5$	1990	1987	1957	1955	2008	{2017	1972	{1987	2004	2004	1969	1967
$\nu_1 + \nu_3$	2008	2009	1976	1980		2023		1982				
$\nu_1 + \nu_6$									2092	{2084	2024	2025
$2\nu_2$	2070	{2046	2038		2079	2088	2079	2090		2086	2101	2092
$A + B + C$...		2053 †	2066	2053 †								
$2B + C$									2114	2113 ‡	2119	2115 ‡
$2\nu_5 + A$					2309	2292 *	2299	2294 *				
$\nu_1 + \nu_2$	2299	2299	2268	{2263					2331	2337	2315	2312
$\nu_4 + \nu_6$	2326	2339		2281								
?											2347	
?											2457	
?											2538	
$2\nu_1$	2545	2552	2494	2488								
$2\nu_6 + B$	2571	2566	2538	2524	2571	2553	2519	2513				
$\nu_2 + \nu_4$					2591	2591	2571	2564				
$A + B + \nu_3$...									2558	2567 §	2564	2565 §

* Assuming A = 880 cm.$^{-1}$. † Calc. for $CsUO_2(NO_3)_3$, using frequencies in the fluorescence spectrum. ‡ Assuming C = 213 cm.$^{-1}$. § Assuming A = 874 cm.$^{-1}$, as in the fluorescence spectrum. Figures in braces are alternative assignments.

Only three combination frequencies and one overtone were observed in the uranyl nitrate hexahydrate spectrum: the frequencies and their probable assignments are given in Table 5.

Nitrogen-isotope Shifts.—For an isolated nitrate ion ν_1 should not shift on nitrogen-isotope substitution, since the nitrogen atom is stationary in this mode. For a co-ordinated nitrato-group there will be a small movement of the group as a whole and a small nitrogen-isotope shift. In Dieke and Duncan's fluorescence spectrum of cæsium uranyl nitrate, shifts of 1·2 and 1·1 cm.$^{-1}$ respectively were observed in a pair of frequencies at 1020·8 and 1025·2 cm.$^{-1}$ which we assign to this mode. Such shifts would not be detected in our infrared spectra.

TABLE 4. $UO_2(NO_3)_2,6H_2O$. *Fundamentals.*

	ν_1	ν_2	ν_3	ν_4	*A*	*A* *	*B*	*B* *	$\nu_2(H_2O)$	H_2O
^{14}N	1030	803 835	1366	748	865 sh	864	941	941	1629	3270 3470 3650
^{15}N	1031	784 814	1339	747	866 sh		943		1629	—

* Values taken from Dieke and Duncan's fluorescence spectrum.
— Not studied.

TABLE 5. $UO_2(NO_3)_2,6H_2O$. *Overtones and combinations.*

	A + *B*		$\nu_2 + \nu_3$		$3\nu_2$		$2\nu_2 + B$	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
^{14}N	1806	1802	2169	2146	2505	2494	2547	2551 sh
^{15}N	1809	1799	2123	2101	2442	2451	2511	2513 sh

The nitrogen-isotope shift in the out-of-plane vibration has been discussed by Decius.[25] Since there is only one vibration of this type the shift is given directly by the Teller–Redlich rule, and the experimental values in the infrared and the fluorescence spectra of the uranyl nitrates correspond closely with the calculated values.

The two degenerate vibrations of the nitrate ion, ν_3 and ν_4, are of the same symmetry type, and the individual isotope shifts may be calculated only by assuming a particular dynamical model. No such calculation has been published, but Pryce[26] has made a calculation assuming a model having in-plane restoring forces of three types, (1) along the N–O bonds, (2) along lines joining pairs of oxygen atoms, and (3) an angle-dependent force for each O–N–O angle. This calculation predicts shifts for ν_3 and ν_4 of 29—33 cm.$^{-1}$ and 2—4 cm.$^{-1}$ respectively.

In dinitrogen pentoxide[27] and uranyl nitrate hexahydrate ν_3 is observed to shift by about 30 cm.$^{-1}$ and there is no detectable shift of ν_4. In the spectra of the uranyl nitrates having co-ordinated nitrato-groups these vibrations behave similarly; ν_1 and ν_4 each shift by 30—40 cm.$^{-1}$ and no shifts are observed for ν_3 and ν_5.

The fluorescence spectrum of cæsium uranyl nitrate follows this pattern with ν_3, ν_4, and ν_5 (assigned to Dieke and Duncan's lines *E* and *F*, *J* and *K*, and *G* and *H* respectively), but not with ν_1 (with assignment of Dieke and Duncan's lines I_3 and I_4 to $^{14}NO_3$ and I_2 and I_5 to $^{15}NO_3$) whose components have only half the expected shifts. This apparent discrepancy between the fluorescence and the infrared spectra may be due to our having used a sample of higher ^{15}N-enrichment (82 atoms % ^{15}N, compared with Dieke and Duncan's 70%): mutual interaction between the three nitrato-groups of each trinitratouranyl ion, when mixed isotopes are used, might reduce the apparent isotope effect.

The interpretations of the band splittings observed in these spectra, and the isotope shifts were based on original suggestions by Professor M. H. L. Pryce, F.R.S., whose help we gratefully acknowledge. We are also indebted to Dr. D. J. Millen and Dr. W. A. Runciman for valuable discussions, to Mr. T. F. Johns, for the gift of ^{15}N, and to Mr. A. M. Deane for recording the spectrum obtained with the Hilger instrument.

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[26] M. H. L. Pryce, personal communication.

[27] Teranishi and Decius, *J. Chem. Phys.*, 1954, **22**, 896.