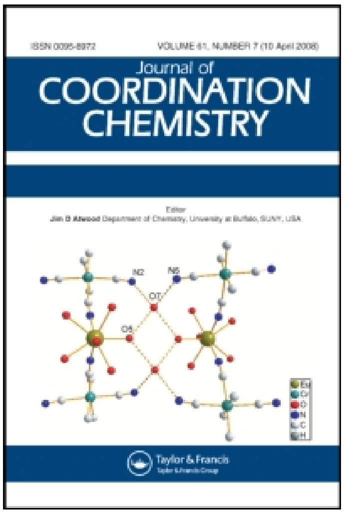

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INFRARED SPECTROSCOPIC STUDIES OF SOME URANYL NITRATE COMPLEXES

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The infrared spectra of ammonium, potassium, rubidium and cesium uranyl trinitrates ($NH_4UO_2(NO_3)_3$, $KUO_2(NO_3)_3$, $RbUO_2(NO_3)_3$ and $CsUO_2(NO_3)_3$) have been measured in the region from 4000 cm^{-1} down to 30 cm^{-1}. A normal coordinate analysis of the complexes has been made as a six-body problem $(UO_2X_3)^-$ ($X = NO_3^-$) neglecting the outer cations. Force constants of U–O and U–X bonds in $UO_2X_3^-$ anion have been approximately obtained on the basis of a modified valence force field including an additional force constant of opposite U–O bond-bond interaction. In addition, bond order of the uranyl bonds of the complexes has been determined from the U–O stretching force constants and compared with those of other uranium compounds such as metal uranates and uranium oxides.

INTRODUCTION

The vibrational studies of a series of uranyl complexes have been made by many investigators[1–8]. According to them, it has been customary that the vibrational analysis of the uranyl complexes is made on the assumption of uranyl ion (UO_2^{2+}) having a linear triatomic structure. In particular, much attention has been paid to the relationahip between the uranyl bond lengths and stretching force constants[3,4,5,8], as well as the ligation effects on the vibrational spectrum of the uranyl ion.[4,6] In order to obtain a more detailed information on the characteristics of the complexes, it is necessary to perform a thorough vibrational analysis including the ligands and the outer cations, differing from the analysis pointed out in the beginning. Although it is difficult to perform such analysis at present since the exact structural parameters of most complexes are lacking, an approximate analysis which is worthy to be considered on the understanding of the physical and chemical properties of the complexes can be made.

In the present study, we have measured the infrared spectra of ammonium, potassium, rubidium and cesium uranyl trinitrates ($NH_4UO_2(NO_3)_3$, $KUO_2(NO_3)_3$, $RbUO_2(NO_3)_3$ and $CsUO_2(NO_3)_3$) and made a preliminary normal coordinate analysis of the complexes as a six body problem $(UO_2X_3)^-$.† On the basis of the analysis, some of the lower bands observed below 1000 cm^{-1} have been assigned to the respective vibration modes expected from the assumption of $(UO_2X_3)^-$. In addition to these, bond order of the uranyl bonds of the complexes has been determined through the U–O stretching force constants and compared with those of other uranium compounds such as metal uranates and uranium oxides.

EXPERIMENTAL

Preparation of the Complexes

The method of preparation of the ammonium, potassium, rubidium and cesium uranyl trinitrates, general formula $M^IUO_2(NO_3)_3$, are based on those described by Meyer *et al.*[9] and Ryan.[10]

The stoichiometric quantities of uranyl nitrate hexahydrate (Yokosawa Chemical Co. Ltd., Japan, GR grade) which was recrystallized before use was added to the solutions of ammonium, potassium, rubidium and cesium nitrates. The mixtures were evaporated and then dried at 80°C–90°C overnight. The complexes obtained thus were identified by infrared spectral measurements.

Spectroscopic Technique

Absorption measurements in the rocksalt and potassium bromide regions were made with a JASCO-IRA2 type grating spectrometer (4000–

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†This approximate analytical method can be supported by the references, for example, T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, 18, 89 (1962).

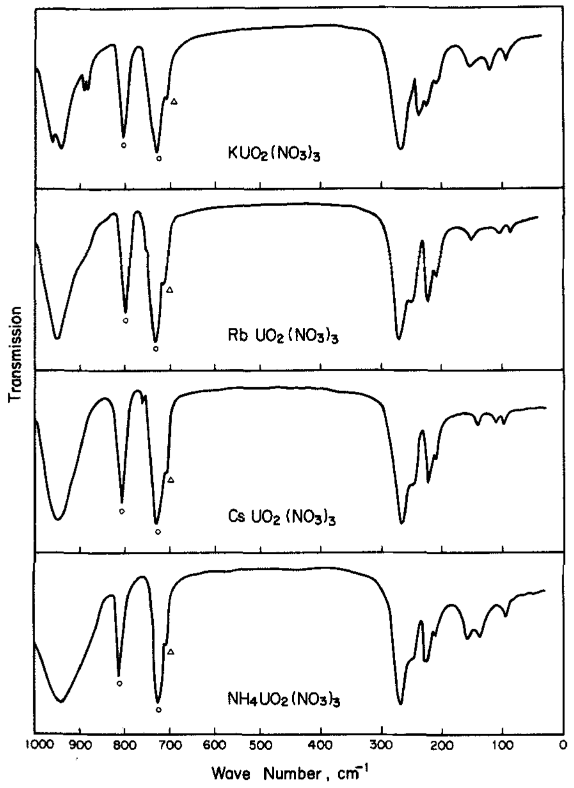

FIGURE 1 Infrared spectra of uranyl nitrate complexes in the region below 1000 cm^{-1}
○. . . . peaks due to nitrate group
Δ. . . . peak due to Nujol

400 cm^{-1}) on nujol and fluorube mulls using KRS-5 cells. Far-infrared absorption measurements were also made at room temperatuer with a JASCO-DS-601G type grating spectrometer (500–30 cm^{-1}) on nujol mulls placed between thin polyethylene films. The results below 1000 cm^{-1} are shown in Fig. 1.

RESULTS AND DISCUSSION

Tentative Assignments of the Observed Bands

Fundamental vibrations Toping[6] and Bullock[7] have tentatively made the vibrational assignments of the uranyl nitrate complexes in the rocksalt and potassium bromide regions. The fundamental vibrational modes of the nitrate group in the complexes have been determined from the assumption of the C_{2v} point group, for which the nitrate group has six infrared-active fundamental vibrations ($3A_1 + B_1 + 2B_2$), rather than D_{3h} symmetry. The bands observed in the region from 1600 cm^{-1} to 700 cm^{-1}, excluding two bands at near 880 cm^{-1} (weak) and 960 cm^{-1} (strong), have been assigned reasonably to six fundamental modes of the nitrate group by Bullock[7]. In the present investigation, we also obtained six characteristic absorption peaks, assignable to six fundamental modes of the nitrate group. The results were omitted to avoid the repitition.

As is well known, the uranyl group in the complexes has a colinear O–U–O structure belonging to the point group $D_{\infty h}$, so that three fundamental vibrational modes are expected; the symmetric stretching (Σ_g^+), antisymmetric stretching (Σ_u^+) and the doubly-degenerate bending vibrations (Π_u). The former one is Raman-active and infrared forbidden, but often appears as a weak absorption in the infrared spectral region of 800–900 cm^{-1}. For $KUO_2(NO_3)_3$ of the uranyl nitrate complexes, corresponding band has been observed as a weak doublet at 872 and 877 cm^{-1} as shown in Fig. 1. From a consideration of the fact that this band occurs only in the crystal, it seems most reasonable to conclude that the appearance of this band results from the crystal field effects which cause the symmetry lowering of the whole ion; that is, lead partly to the nonlinearlity and/or nonequivalence of the uranyl bonds (O–U–O). However, for other three complexes, no band has been observed clearly in this region. The latter two of the antisymmetric stretching and the bending vibrations are infrared active and occur in the regions of 900–1000 cm^{-1}, and 250–270 cm^{-1}, respectively. As seen from Fig. 1, all the complexes have a weak shoulder (250 cm^{-1}) on the low-freqnency edge of the doubly-degenerate bending vibration at 265–267 cm^{-1}. These observations may be understood when considering the crystal field effects as foregoing interpreted.

On the assumption of $UO_2X_3^-$ (point group D_{3h}) as will be discussed later in detail, three bands as described above just correspond to the species A_1' (symmetric stretching vibration), A_2'' (antisymmetric stretching vibration) and E' (doubly-degenerate bending vibration).

Similar phenomenon to the doubly-degenerate beinding vibration also occurs in the far-infrared region from 240 cm^{-1} to 210 cm^{-1} as shown in Fig. 1. The bands observed in this region can be assigned mainly to the U–O(NO_2) strethcing vibration[12], in other words, the U–X stretching vibration corresponding to the species E'.

In the region below 200 cm^{-1}, three bands have been observed at near 150, 120 and 90 cm^{-1} for each complex as shown in Fig. 1. By taking into account the results of an approximate normal coordinate analysis as will be described later, the 150 cm^{-1} band is somewhat arbitrarily assigned to the X–U–X bending vibration corresponding to the E′ species and the 120 cm^{-1} band to the X–U–O bending vibration corresponding to the A″ species. However, in order to assign exactly these bands, some additional experimental evidence is necessary and will be reported at a later date. The weak band at near 90 cm^{-1} may be assigned undoubtedly to the lattice vibration resulting from the interaction between the $UO_2X_3^-$ and M^+ (NH_4, K, Rb, Cs) ions by considering its location.

Overtone and combination bands The most part of the overtone and combination bands of the uranyl nitrate complexes have been observed in the higher region above 1600 cm^{-1}. For example, $KUO_2(NO_3)_3$ has eleven absorption peaks at 2545, 2520, 2288, 2262, 2041, 1980, 1840, 1818, 1765, 1730 and 1606 cm^{-1}. All these bands are tentatively ascribed to the overtones and combinations of the nitrate and uranyl groups. The detailed assignments of each band followed that of Bullock.[7]

It is interesting to note the combination band which occurs as a sharp, narrow peak at 1830 cm^{-1} for $NH_4UO_2(NO_3)_3$, 1818 cm^{-1} for $KUO_2(NO_3)_3$, 1833 cm^{-1} for $RbUO_2(NO_3)_3$ and 1827 cm^{-1} for $CsUO_2(NO_3)_3$. These bands are assignable definitely to the combinations of the symmetric and anti-symmetric stretching vibrations of the uranyl group. In other words, on the assumption of $UO_2X_3^-$ ion, these bands correspond to the $A_1' + A_2'$ which should be infrared-allowed.

Normal Coordinate Analysis

In beginning an approximate normal coordinate analysis of the uranyl nitrate complexes, it is appropriate to assume that the complexes contain the discrete $UO_2(NO_3)_3^-$ ions. The structure of $UO_2X_3^-$ ($X = NO_3$) is known to be reasonably close to that in Fig. 2, wherein the nitrate groups are arranged in a plane equatorial to the O–U–O axis.[4] It is presumed then that the relevant spectroscopic entity is the D_{3h} structure of Fig. 2. It is shown by the group theoretical consideration that for the $UO_2X_3^-$ ion, there are eight fundamental vibrations, i.e. two A_1' (Raman-active), two A_2'' (infrared-active), three E′ (infrared-active) and one E″ (Raman-active) vibrations.

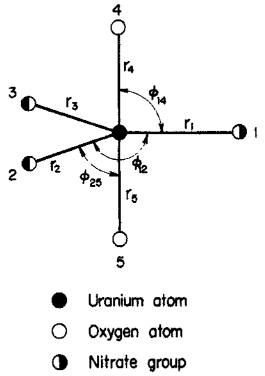

FIGURE 2 Internal coordinates for $UO_2X_3^-$ ion assumed in uranyl nitrate complexes (point group: D_{3h})

The internal coordinates for the discrete $UO_2X_3^-$ ion are defined in Fig. 2. A potential function of the modified valence force field has been used:

$$V = \tfrac{1}{2}\Sigma K_i(\Delta r_i)^2 + \tfrac{1}{2}\Sigma H_{ij}(r_i r_j \Delta\phi_{ij})^2 + \text{(additional term due to additional force constant)} \qquad (1)$$

where K and H are the force constants for the bond stretching and angle deformation. The potential function also includes the additional term due to one additional force constant of the opposite U–O bond-bond interaction. In order to obtain the vibrational kinetic energy with the internal coordinates, the method developed by Wilson[11] is used and the norma normal vibrations can be calculated from the secular equation,

$$|GF - E\lambda| = 0 \qquad (2)$$

where E is the unit matrix and $\lambda = 4\pi^2C^2\nu^2$.

In the frequency calculations, total mass of the NO_3 group was used as that of X and the force constants were adjusted so as to give the best agreement between the observed and calculated frequencies. The results are shown in Table I, in which K_1 and K_2 are the force constants for the bond stretching of U–X and U–O, H_1 and H_2† those for the bond angle deformation X–U–X and X–U–O and k that for the opposite U–O bond-bond interaction. It should be noted that the stretching force constant of the U–O bond is very large as compared with other force constants. This means that the bond length of U–O is relatively short.

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†Without using directly the bond distances, the force constant H_2 was first adjusted as $(r_1/r_0)H_2 = A$ and $(r_0/r_1)H_2 = B$, where r_0 and r_1 are the equilibrium bond distances of the U–X and U–O bonds. The ratio $r_1^2/r_0^2 = A/B$ was then calculated, from which the H_2 was determined.

TABLE I
Force constants (md/Å) of $UO_2X_3^-$ ion assumed in uranyl nitrate complexes

	$KUO_2(NO_3)_3$	$RbUO_2(NO_3)_3$	$CsUO_2(NO_3)_3$	$NH_4UO_2(NO_3)_3$
K_1	2.000	1.949	1.833	1.949
K_2	7.451	7.420	7.370	7.370
k	−0.201	−0.154	−0.203	−0.120
H_1	0.450	0.404	0.448	0.463
H_2	0.139	0.128	0.120	0.145

Jones[3] has pointed out that application of Badger's rule to force constants calculated from infrared spectrum permits an evaluation of the uranyl bond distance (R_{U-O}).

$$R_{U-O} = 1.08\,K^{-1/3} + 1.17 \qquad (3)$$

It is shown by this relationship that the bond length of U–O are in a range of 1.72–1.73 Å. A further point of interest is that the additional force constant defined as the U–O bond-bond interaction is of a negative sign. This negative value indicates that in the complex it is easier to lengthen or to shorten both U–O bonds simultaneously than it is to lengthen one bond and to shorten the other. This feature of the complexes sets it apart from linear symmetric triatomic molecules such as carbon dioxide and carbon disulfide of which valence bond descriptions seem to yield positive values for the bond-bond interaction constant.

The calculated frequencies are listed in Table II as compared with the observed ones. In this Table, Raman data in the far infrared region which have been measured by Bullock, *et al.*[12] are also given. The agreement between the observed and calculated frequencies is satisfactory.

Bond Order of Uranium–Oxygen Bond

The order of U–O bond in the uranyl nitrate complexes is considerably affected with the nature of ligands coordinated to uranium atom and/or of outer cations. Although changes in the bond orders can be supposed to some extent by consideration of the U–O stretching force constants, it has not been made to explain these quantitatively. It is therefore of very interest to give a quantitative interpretation for this problem.

In determining the order of U–O bond in the

TABLE II
Observed and calculated frequencies (cm^{-1}) of uranyl nitrate complexes

		$KUO_2(NO_3)_3$		$RbUO_2(NO_3)_3$		$CsUO_2(NO_3)_3$		$NH_4UO_2(NO_3)_3$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
A_1'	ν_1	877 (872)	877	878[b]	878	872[b]	872	880[b]	880
	ν_2	234[a]	234	231[a]	231	224[a]	224	231[a]	231
A_2''	ν_3	960 (948)	960	955	955	955	955	950	950
	ν_4	120	120	107	107	116	116	138	138
E′	ν_5	237 (227) (210)	210	224 (213)	201	220 (212)	206	224 (213)	210
	ν_6	267 (250)	294	267 (250)	288	265 (250)	283	267 (250)	291
	ν_7	150	140	150	143	142	126	155	128
E″	ν_8	168[a]	168	166[a]	166	154[a]	154[a]	166[a]	166

[a] These were calculated from the observed combination bands ($A_1' + A_2''$).
[b] See Ref. 12.

TABLE III
Bond order of uranium–oxygen bonds of uranyl nitrate complexes, metal uranates and uranium oxides

	U–O stretching force constant (md/Å)	Bond length (Å)	Bond order
UO_2F_2	8.13	1.71	1.000
$KUO_2(NO_3)_3$	7.451	1.72	0.894
$RbUO_2(NO_3)_3$	7.420	1.72	0.894
$CsUO_2(NO_3)_3$	7.370	1.73	0.805
$NH_4UO_2(NO_3)_3$	7.370	1.73	0.805
K_2UO_4	4.44	1.84 ($U–O_I$)	0.345
	1.19	2.17 ($U–O_{II}$)	0.053
Rb_2UO_4	4.34	1.84 ($U–O_I$)	0.345
	1.06	2.18 ($U–O_{II}$)	0.050
Cs_2UO_4	4.38	1.84 ($U–O_I$)	0.345
	0.835	2.19 ($U–O_{II}$)	0.046
δ–UO_3	2.48	2.075	0.095
UO_2	1.05	2.37	0.000

uranyl nitrate complexes, it is convenient to start with a π-electron theory previously developed by Coulson and Longuet-Higgins,[13,14] who has applied it to unsaturated hydrocarbons. When the theory is applied to any change of configuration in the uranyl bond, the potential energy change is formally written as

$$\delta V = \delta F + \delta E, \tag{4}$$

where F is the energy of the σ-bonds and E the total energy of the π-electrons. Here, if we ignore changes in energy due to angular distortion, and interactions between different σ-bonds the energy of the σ-bonds may be given by

$$F = \sum_n \tfrac{1}{2} K\sigma (R_n - r)^2, \tag{5}$$

where K_σ and r are the force constant and distance of pure σ-bond, and R_n is the distance of the nth bond. E, on the other hand, is most conveniently expressed as a function of the resonance integrals of the unsatulated bonds, resonance integral β_n of the nth bond depending only on its distance R_n. For this dependence, a following relationship has been assumed by Lennard-Jones,

$$2\beta_n = \text{const.} + \tfrac{1}{2}K(R_n - d)^2 - \tfrac{1}{2}K_\sigma(R_n - r)^2, \tag{6}$$

where K and d are the force constant and distance of a pure double bond. Using a following definition by Coulson and Longuet-Higgins,[15]

$$\left(\frac{\partial E}{\partial \beta_n}\right)_{\bar{R}} = 2P_n, \tag{7}$$

the order of nth bond P_n is finally obtained as

$$P_n = \frac{-K_\sigma(\bar{R}_n - r)}{K(\bar{R}_n - d) - K_\sigma(\bar{R}_n - r)}, \tag{8}$$

where $\bar{R}$ is the equilibrium bond distance.

Before determining the order of U–O bonds in the complexes by the use of equation (8), we must select the values of K, d and K_σ, r. For the former K and d, we may use the experimental values (K = 8.13 md/Å, d = 1.71 Å) of uranyl fluoride, UO_2F_2,[16] since the fluorine atoms in the compound have a large electronegativity and, therefore, the uranyl bond seems to be double. The adoption of such values is also regarded as being reasonable from the fact that the force constant of U–O stretching in uranyl fluoride is the largest in uranyl compounds measured so far. For the latter K_σ, r, on the other hand, we take the values (K_σ = 1.05 md/Å, r = 2.37 Å) of uranium dioxide (cubic)[17] having infinite chain structure of –O–U–O–U–, in which the uranium and oxygen atoms are jointed by the σ-bonds. Inserting these values to equation (8), we obtain

$$P_n = \frac{-1.05(\bar{R}_n - 2.37)}{8.13(\bar{R}_n - 1.71) - 1.05(\bar{R}_n - 2.37)}. \tag{9}$$

Now if we put the equilibrium U–O distances of uranyl nitrate complexes in equation (9), the order of U–O bonds can be directly determined.

In the case of the complexes, we have used as the equilibrium U–O distances the values calculated from the U–O stretching force constants by the use of Badger's rule,[3] since their experimental values are lacking. The results of the complexes are listed in Table III, together with those of other metal uranates and uranium oxide. It is found from the table that the uranyl bonds of the complexes hold almost the double bond configuration, the primary bonds of the metal uranates have just intermediate configuration between the single and double bonds, while the secondary bonds of the uranates are the single ones. In the case of δ-uranium trioxide, it is also found that all the bonds have the single bond configuration as suggested from the crystal structure.

REFERENCES

1. B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 3965 (1958).
2. L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958).
3. L. H. Jones, *Spectrochim. Acta*, **11**, 409 (1959).
4. S. P. McGlynn, J. K. Smith and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961).

5. H. R. Hoekstra, *Inorg. Chem.*, **2**, 492 (1963).
6. G. Topping, *Spectrochim. Acta*, **21**, 1743 (1965).
7. J. I. Bullock, *J. Inorg. Nucl. Chem.*, **29**, 2257 (1967).
8. J. I. Bullock, *J. Chem. Soc. (A)*, 781 (1969).
9. R. J. Meyer and F. Wendel, *Ber.* **36**, 4055 (1903).
10. J. L. Ryan, *J. Phys. Chem.*, **65**, 1099 (1961).
11. E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill, New York (1955).
12. J. I. Bullock and F. W. Parrett, *Can. J. Chem.*, **48**, 3095, (1970).
13. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. A*, **193**, 456 (1948).
14. H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.*, **48**, 1077 (1952).
15. C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. A*, **191**, 39 (1947).
16. K. Ohwada, *J. Inorg. Nucl. Chem.*, **33**, 1615 (1971).
17. M. Tsuboi, M. Terada and T. Shimanouchi, *J. Chem. Phys.*, **36**, 1301 (1962).