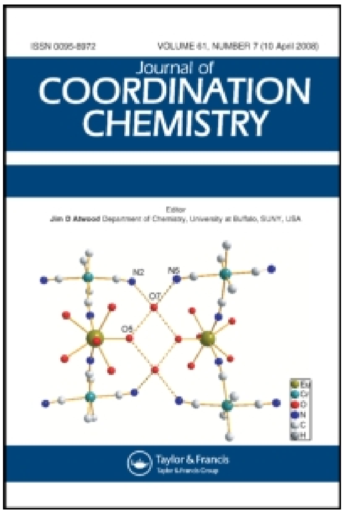

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RAMAN SPECTROSCOPIC STUDIES OF SOME URANYL NITRATE COMPLEXES

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RAMAN SPECTROSCOPIC STUDIES OF SOME URANYL NITRATE COMPLEXES

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Laser Raman spectra of uranyl trinitrate complexes ($KUO_2(NO_3)_3$, $RbUO_2(NO_3)_3$, $CsUO_2(NO_3)_3$, $NH_4UO_2(NO_3)_3$) have been measured in the region from 2000 cm^{-1} to 10 cm^{-1}. Vibrational assignments have been made on the assumption that all the complexes contain discrete $UO_2X_3^-$ ($X = NO_3$) ions belonging to a point group of D_{3h}.

A brief discussion is made on the ligation effect of nitrate group on the uranyl bond order from a point of view of molecular orbital theory.

INTRODUCTION

Recently, we have reported on the infrared spectra of some uranyl trinitrate complexes, wherein vibrational assignments and normal coordinate analyses for the spectra are made in detail and besides an empirical equation is proposed to determine bond orders of the uranium–oxygen (U–O) bonds of the complexes through the U–O stretching force constants.[1] Unfortunately, we have been unable to add detailed assignments for the Raman spectra of the complexes to the previous paper[1] for lack of our spectral data. Therefore, it seems valuable to measure the Raman spectra of the complexes and give the vibrational assignments for such spectra.

In the present study, laser Raman spectra of $KUO_2(NO_3)_3$, $RbUO_2(NO_3)_3$, $CsUO_2(NO_3)_3$ and $NH_4UO_2(NO_3)_3$ have been measured in the region from 2000 cm^{-1} to 10 cm^{-1}. The assignments for the observed frequencies of the complexes have been made in the same manner as described in the previous paper.[1] Much attention has been paid to the ligation effect of nitrate group on the uranyl bond order. In particular, a bond order – bond length relationship previously proposed without any confirmation has been justified on the basis of reduction behaviour of the uranyl ions and molecular orbital theory.

EXPERIMENTAL

Preparative Methods

The preparation of the uranyl trinitrate complexes was described elsewhere.[1-2]

Raman Spectroscopic Measurements

Raman spectra of the solid complexes sealed in the glass tube (i.d.: 2 mm, length: 90 mm) were obtained in the region from 2000 cm^{-1} to 10 cm^{-1} using a JASCO R-800 type Laser Raman spectrometer. The 5145 Å line of a Ar^+ laser (SP-164-00 type, power: 200 mw) was used for excitation. The frequencies quoted are accurate to 0.2 cm^{-1}. In spite of all the complexes being fluorescent, relatively high quality Raman spectra were obtained. A typical example of $NH_4UO_2(NO_3)_3$ is shown in Figure 1.

RESULTS AND DISCUSSION

Before discussion of the results, let us assume that the complexes contain the discrete $UO_2X_3^-$ ($X = NO_3$) ion whose relevant spectroscopic entity is the D_{3h} structure. A group theoretical consideration shows 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. Only the Raman-active vibrational modes along the symmetry coordinates are approximately shown in Figure 2.

Tentative Assignments of the Observed Bands

Fundamental vibrations of the $UO_2X_3^-$ ion All the Raman frequencies observed for the complexes in the region from 2000 to 10 cm^{-1} are listed in Table Ia, wherein tentative assignments for those are given. For completeness, the infrared frequencies are also listed

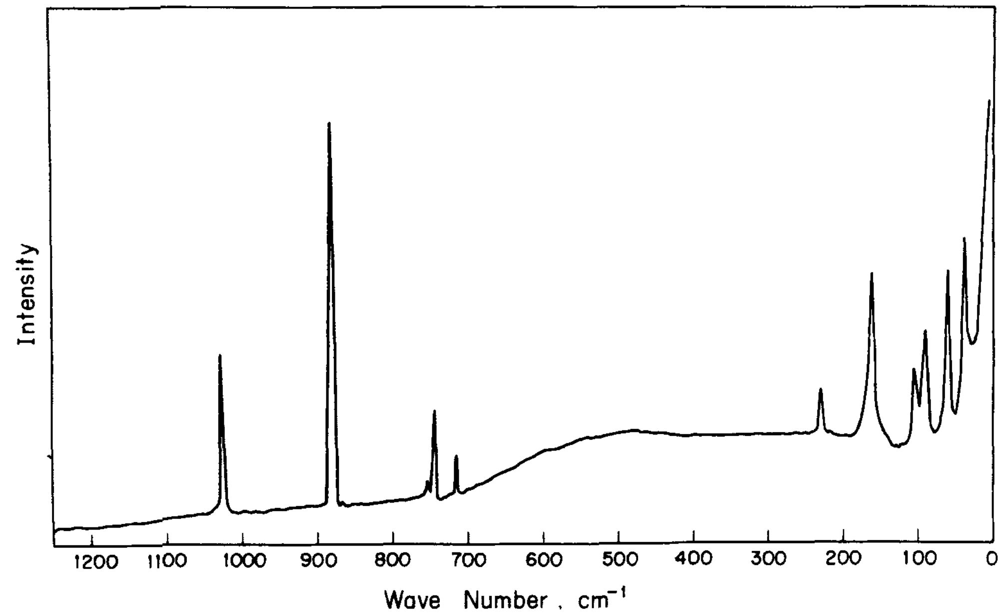

FIGURE 1 Laser Raman spectra of ammonium uranyl trinitrate ($NH_4UO_2(NO_3)_3$).

in Table Ib.[1] The Raman-active fundamental vibrations arising from the $UO_2X_3^-$ ion are

$$2\,A_1' + E'',$$

where $2A_1'$ are the symmetric U–O and U–X stretching vibrations and E'' is the symmetric O–U–X bending vibration (see Figure 2). It is characteristic that the symmetric U–O stretching vibration occurs in relatively high frequency region (800 ~ 900 cm^{-1}) and, moreover, as a strong band.[3] Therefore, the bands observed at near 880 cm^{-1} for all the complexes can be assigned to this vibration (A_1' : ν_1) as shown in Table 1a. On the other hand, it is expected that the symmetric U–X stretching vibration occurs in rather low frequency region, but in definitely higher than the O–U–X bending vibration frequency.[4] Accordingly, the bands observed at 224 ~ 235 cm^{-1} are assignable to the symmetric U–X stretching vibration (A_1' : ν_2) and those at 151 ~ 166 cm^{-1} to the O–U–X bending vibration (E'': ν_8). The above assignments for three Raman-active vibrational modes of the $UO_2X_3^-$ ion may also be supported from a normal coordinate analysis as described in the previous paper.[1]

Fundamental vibrations of the nitrate group The vibrational assignments for the infrared-active bands of the nitrate group in the complexes have been made, in detail, on the assumption of the C_{2v} point group rather than D_{3h} symmetry by several authors.[2,5]

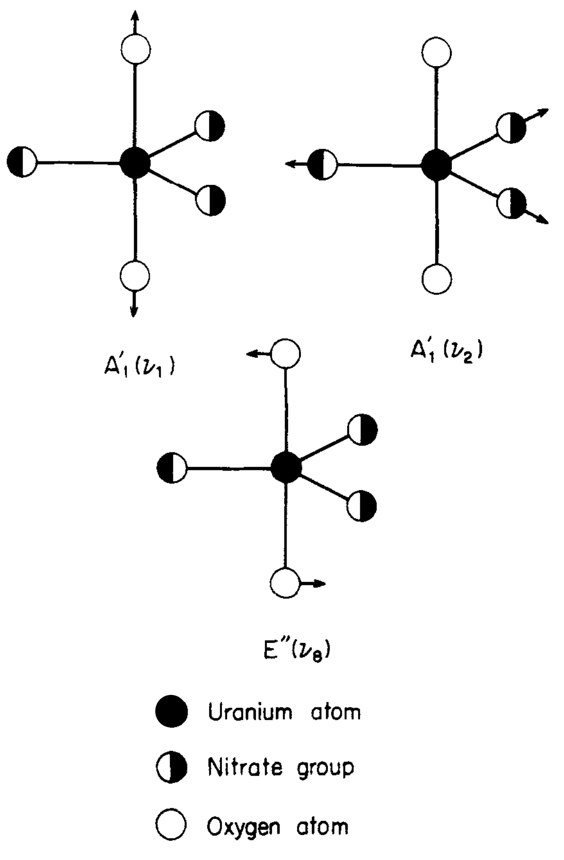

FIGURE 2 Approximate modes of only the Raman-active vibrations.

TABLE Ia
Observed Raman frequencies of some uranyl nitrate complexes and their assignments

$KUO_2(NO_3)_3$	$RbUO_2(NO_3)_3$	$CsUO_2(NO_3)_3$	$NH_4UO_2(NO_3)_3$	Assignment
1605 vw	–	1605 vw	1606 vw	Overtone (NO_3
1520 vw	1515 vw	1513 vw	1511 vw	Fundamentals (NO_3)
1032 m	1025 m	1025 m	1027 m	
874 s	880 s (860) m	880 s	880 s	A_1' (ν_1), Fundamental
–	747 w	746 vw	749 vw	Fundamentals (NO_3)
744 w	740 w	740 w	742 w	
716 vw	–	713 vw	715 vw	
235 w	227 w	224 w	230 w	A_1' (ν_2), Fundamental
166 m	151 m	151 m	163 m	E''(ν_8), Fundamental
108 w	103 w	100 sh	105 w	Lattice modes
80 w	90 m	90 m	90 w	
58 w	59 m	46 m	60 m	
25 m	35 m	34 w	36 m	

s: strong, m: medium, w: weak, vw: very weak, sh: shoulder.

TABLE Ib
Infrared-active fundamental vibrations of $UO_2X_3^-$ ion assumed in uranyl trinitrate complexes[1]

Species	$KUO_2(NO_3)_3$	$RbUO_2(NO_3)_3$	$CsUO_2(NO_3)_3$	$NH_4UO_2(NO_3)_3$
A_2'' ν_3	960 (948)	955	955	950
ν_4	120	107	116	138
E' ν_5	237 (227) (210)	224 (213)	220 (212)	224 (213)
ν_6	267 (250)	267 (250)	265 (250)	267 (250)
ν_7	150	150	142	155

According to the assumption of the C_{2v} symmetry, it is expected for the nitrate group that all the six fundamental vibrations,

$$3\,A_1 + B_1 + 2\,B_2,$$

are both infrared- and Raman-active. From the similarity to the assignments for the infrared-active bands, the Raman bands observed in the region from 1600 cm^{-1} to 700 cm^{-1}, excluding one band at near 880 cm^{-1} (strong) can be assigned reasonably to the fundamental modes of the nitrate group as shown in Table II. However, as seen from Table II, the $B_1(\nu_4)$ and B_2 (ν_6) bands are absent for all the complexes and even the B_2 (ν_5) band for $RbUO_2(NO_3)_3$. There are two probable reasons why these bands are not observed clearly. One is that Raman intensities of the bands, in other words, changes in polarizabilities of the complexes, may be very small. Another is that the assumption of the C_{2v} point group may be inadequate for the nitrate group. However, it seems reasonable to prefer the former rather than the latter, since the infrared absorption bands observed for the nitrate group can be satisfactorily explained on the assumption of the C_{2v} point group.[1, 2, 5] To give further information on this question, more sensitive measurements of the Raman spectra of the complexes will be necessary.

Other vibrations For all the complexes besides $RbUO_2(NO_3)_3$, a very weak band occurs in fairly high frequency region above 1600 cm^{-1} as shown in Table 1a. This band may be assigned to an overtone arising from the fundamental vibration B_2 (ν_6) of the nitrate group.[2] On the other hand, for all the complexes, four bands appear in the lowest frequency region from 110 cm^{-1} to 10 cm^{-1} as listed in Table Ia. Considering their locations, these bands may be described as the lattice vibrations resulting from the

TABLE II
Raman-active fundamental vibrations of the nitrate group in the complexes

Specie		$KUO_2(NO_3)_3$	$RbUO_2(NO_3)_3$	$CsUO_2(NO_3)_3$	$NH_4UO_2(NO_3)_3$
A_1	ν_1	1520	1515	1513	1511
	ν_2	1032	1025	1025	1027
	ν_3	744	747 (740)	747 (740)	749 (742)
B_1	ν_4	–	–	–	–
B_2	ν_5	716	–	713	715
	ν_6	–	–	–	–

interaction between the $UO_2X_3^-$ and M^+ (K, Rb, Cs, NH_4) ions. Unfortunately, we must postpone the group-theoretical prediction of the lattice vibrational modes at the present stage, since the crystallographic data on the complexes is lacking.

Justification of a Bond Order – Bond Length Equation

The order of a U–O bond in the uranyl complex is considerably affected by the nature of the ligands coordinated to uranium atom as well as of outer cations. To obtain knowledge of the U–O bond orders in various uranyl complexes, we have previously proposed, without any confirmation, an empirical equation;[1]

$$P_n = \frac{-1.05(\bar{R}_n - 2.37)}{8.13(\bar{R}_n - 1.71) - 1.05(\bar{R}_n - 2.37)}, \qquad (1)$$

where P_n is the U–O bond order and $\bar{R}_n$ is the equilibrium U–O bond length. If here we can give some justification to Eq. (1), it will be of great use for obtaining much information on the changes in the uranyl bond order as well as the ligation effects on the uranyl bond strength.

For this purpose, it is convenient to start from consideration of electron configurations of the uranyl species, UO_2^{2+}(VI), UO_2^+(V), etc. The electron configuration of ground state of UO_2^{2+}(VI) may be written by the same molecular orbital notation as Ref. (6) and (7) as follows:

$$UO_2^{2+}(VI) \quad (1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4.$$

If the successive reductions of UO_2^{2+}(VI) occur, the electrons are populated one by one on the atomic-like molecular orbitals of higher energy levels, i.e.

$$UO_2^+(V) \quad (1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4(\Phi_u)^1,$$

$$UO_2(IV) \quad (1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4(\Phi_u)^1(\partial_u)^1,$$

$$UO_2^-(III) \quad (1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4(\Phi_u)^1(\partial_u)^1(2\pi_u)^1,$$

$$UO_2^{2-}(II) \quad (1\sigma_u^+)^2(1\sigma_g^+)^2(1\pi_u)^4(1\pi_g)^4(\Phi_u)^2(\partial_u)^1(2\pi_u)^1,$$

where two species of UO_2^-(III) and UO_2^{2-}(II) are the supposed ones and their electron configurations are the same as those of AmO_2^{2+} and AmO_2^+ ions. An approximate diagram of the energy levels is shown in Figure 3, wherein $1\sigma_u^+$, $1\sigma_g^+$ and $1\pi_u$ denote the bonding molecular orbitals, $1\pi_g$ the nonbonding molecular orbital,† and Φ_u, ∂_u and $2\pi_u$ the antibonding molecular orbitals. It is easily found from Figure 3 that the bond order of UO_2^{2+}(VI) is theoretically double, since no electron is populated on the antibonding molecular orbitals of higher energy levels. When the successive reductions of UO_2^{2+}(VI) occur, in other words, the electrons are populated one by one on the antibonding molecular orbitals, we find that the U–O bond order decreases by intervals of 0.25 as listed in Table III.

On the other hand, it should be noted from Table III that the stretching force constants associated with the U–O bonds in the uranyl species decrease gradually with decreasing the theoretical bond orders discussed above. By the way, the force constant of UO_2^{2+}(VI) as listed in Table III is taken from that of UO_2F_2‡[8] since the isolated UO_2^{2+}(VI) is not found, those of UO_2^+(V) and UO_2(IV) are cited from the Refs. (9) and (10), and those of UO_2^-(III) and

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†The orbital of $1\pi_g$ may be described formally as the bonding molecular orbital. However, we can regard the $1\pi_g$ as the nonbonding molecular orbital, because the $1\pi_g$bond is so weak as to be negligible.

‡The adoption of such value is regarded as being reasonable from the facts that the fluorine atoms in UO_2F_2 have a large electronegativity and, moreover, its U–O stretching force constant is the largest in various uranyl compounds measured so far.

TABLE III
U–O bond orders in the uranyl species with various oxidation states

Specie (Oxidation state)	Force constant (md/Å)	Bond distance (Å)	Theoretical bond order	Calculated bond order
UO_2^{2+}(VI)	8.13	1.71	2.00	2.00
UO_2^{+}(V)	6.59	1.74	1.75	1.73
UO_2(IV)	5.26	1.79	1.50	1.48
UO_2^{-}(III)†	3.38	1.89	1.25	1.25
UO_2^{2-}(II)†	1.05	2.37	1.00	1.00

†Although the electron configurations of UO_2^-(III) and UO_2^{2-}(II) are isoelectric with those of AmO_2^{2+} (PuO_2^+) and AmO_2^+, respectively, these species are not yet detected at present.

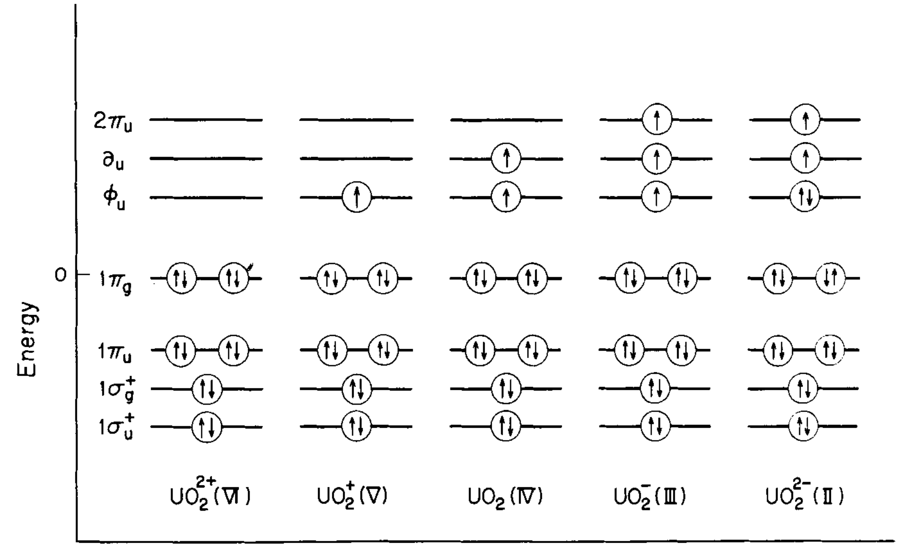

FIGURE 3 Energy diagrams of molecular orbitals for uranyl species.

UO_2^{2-}(II) are estimated by extrapolation.

When we now calculate the U–O bond orders in the uranyl species using the Eq. (1), we require not the U–O force constants but the equilibrium U–O bond lengths. Fortunately, Jones[11] has pointed out that application of Badger's rule to the U–O force constants, K (md/Å) permits an evaluation of the U–O bond lengths, R_{U-O} (Å).

$$R_{U-O} = 1.08\,K^{-1/3} + 1.17 \qquad (2)$$

By this relationship, the U–O bond lengths in the uranyl species can easily be obtained as shown in Table III. Substituting these bond lengths into Eq. (1), we can finally obtain the calculated U–O bond orders as shown in the last column of Table III. Thus we find that the calculated bond orders are in good agreement with the theoretical ones. It may therefore be concluded that Eq. (1) is very useful for determining the U–O bond orders in the uranyl complexes.

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