Vibrational Spectroscopy of Strontium Uranate(VI) Compounds

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The precise nature of strontium uranium oxides has implications for the current understanding of oxygen redistribution after fission. Six strontium uranate(VI) compounds, Sr_3UO_6, Sr_2UO_5, β-$SrUO_4$, $Sr_2U_3O_{11}$, $SrU_4O_{12.8}$, and $SrUO_{3.67}$ have been studied using i.r. spectroscopy and X-ray powder diffraction. Raman spectra have also been obtained for Sr_3UO_6, Sr_2UO_5, β-$SrUO_4$, and $Sr_2U_3O_{11}$. The spectra are presented and discussed and the primary uranium–oxygen bond lengths have been calculated for β-$SrUO_4$, $Sr_2U_3O_{11}$, and $SrU_4O_{12.8}$.

ELEMENTS in Group 2 of the Periodic Table are observed as fission-product inclusions in irradiated UO_2 fuel.[1] In this respect barium has been particularly well characterised, but although strontium is also known to occur its disposition within the fuel is less well understood.[2] Studies using electron-probe microanalysis indicate that strontium is present either as a solid solution of strontium oxide in UO_2 or as a finely dispersed Sr–U–O phase. From their investigation of pseudo-fission products, Koizumi *et al.*[1] considered that the perovskite compound $SrUO_3$ might be formed in which the uranium atom has a formal oxidation state of IV. For uranium, however, the oxidation state VI is generally regarded as the most important and a wide range of ternary uranate(VI) compounds can be readily prepared with Group 2 metals.[3] It is possible [2] that the Sr–U–O phase could be formulated as $Sr_{1-x}U^{VI}{}_{1+x}O_{4-Z}$ where $0 < Z < 1 - x$.

Several spectroscopic studies have been carried out on the uranium–oxygen system,[4,5] but, with the exception of the two i.r. spectra given in a paper by Klíma *et al.*[6] which are titled $SrU_{1.60}O_{5.80}$ and $SrU_{1.57}O_{5.71}$, no vibrational information is available for the Sr–U–O system. We here report a study of the i.r. and Raman spectra of strontium uranate(VI) compounds.

Although compounds of strontium and uranium with oxygen have been known since the nineteenth century,[7] interest in these systems was regenerated in 1948 when Zachariasen [8] published information on the rhombohedral and orthorhombic forms of $SrUO_4$, later termed the α and β forms respectively.[9] Since then the following compounds containing these elements have been reported: SrU_2O_7, SrU_2O_6,[10] $SrUO_{3.4}$, $SrO(1.5$—$1.75)$-UO_3,[11] $Sr_2U_3O_{11}$, $SrU_4O_{12.8}$, $SrUO_{3.3}$, $SrUO_{3.75}$,[9] and $Sr_3U_2O_9$;[12] of these, SrU_2O_7 and SrU_2O_6 have not been prepared recently and may have been mixtures of other uranate compounds.[9] $SrO(1.5$—$1.75)UO_3$ on the other hand was a variable mixture of $Sr_2U_3O_{11}$ and $SrU_4O_{12.8}$ as shown by the published powder-diffraction pattern, while the oxygen-deficient rhombohedral compounds $SrUO_{3.4}$, $SrUO_{3.3}$, and $SrUO_{3.75}$ are probably best grouped together with α-$SrUO_4$, since all four have closely similar X-ray diffraction patterns with only minor differences in cell constants. Detailed structural information is available for rhombohedral $SrUO_4$ [8] and neutron-

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[1] M. Koizumi, M. Satoh, and K. Noro, *J. Nuclear Materials*, 1974, **51**, 90.

[2] C. A. Friskney and K. A. Simpson, *J. Nuclear Materials*, 1975, **57**, 121.

[3] C. K. Keller, *M.T.P. Internat. Rev. Sci.*, *Inorg. Chem. Ser.* 1, 1972, **7**, 47.

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[5] G. C. Allen, J. A. Crofts, and A. J. Griffiths, *J. Nuclear Materials*, 1976, **62**, 273.

[6] J. Klíma, D. Jakeš, and J. Moravec, *J. Inorg. Nuclear Chem.*, 1966, **28**, 1861.

[7] A. Ditte, *Compt. rend.*, 1882, **95**, 990.

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[10] H. R. Hoekstra and J. J. Katz, *J. Amer. Chem. Soc.*, 1952, **74**, 1683.

[11] E. A. Ippolitova, I. A. Bereznikova, V. D. Kosynkin, Yu. P. Simanov, and L. M. Kovba, 'Issledovaniya v Oblasti Khimii Urana,' (ed. V. I. Spitsyn), Moscow, 1961, p. 180 (Translation ANL TRANS-33, Argonne National Laboratory).

[12] C. Brisi, M. Montorsi, and G. A. Burlando, *Rev. Int. Hautes Tempér et Réfract*, 1971, **8**, 37.

diffraction results have been published for β-$SrUO_4$, Sr_2UO_5, and Sr_3UO_6.[13]

EXPERIMENTAL

Preparation of Strontium Uranate(VI) *Compounds*.—All the compounds except $SrUO_{3.67}$ and Sr_2UO_5 were prepared by heating strontium carbonate with U_3O_8, in the appropriate strontium : uranium ratio. The U_3O_8 used in these preparations was obtained by heating commercial UO_2 in air for 48 h at 1 000 °C.

$SrUO_{3.67}$ was made by reducing β-$SrUO_4$ in a stream of hydrogen at 580 °C and Sr_2UO_5 was made by heating equimolar quantities of β-$SrUO_4$ and Sr_3UO_6 at 1 000 °C. A temperature of 850 °C was found to be suitable for all the other preparations except $SrU_4O_{12.8}$ which required 1 000 °C. Heating was carried out in air (except for $SrUO_{3.67}$), for at least 24 h, using a silica boat in an 'Adamel' tube furnace. All the reactions were followed by careful weight measurements, enabling the confirmation of the formula in each case. Preparation of the compound $Sr_3U_2O_9$ was not attempted because of the high temperature required (>1 175 °C).

TABLE 1

Crystal data[a] for strontium uranate(VI) compounds

Compound	Colour[b]	Form	Cell dimension/Å			Angle/°			Space group	Z	Ref.
			a	b	c	α	β	γ			
'α-$SrUO_4$'	Dark grey	Rhombohedral	6.53(3)	6.53(3)	6.53(3)	35.53(33)	35.53(33)	35.53(33)	$R3m$	1	8
β-$SrUO_4$	Bright yellow	Orthorhombic	5.489 6(7)	7.997 0(9)	8.129 7(12)	90	90	90	$Pbcm$	4	13
$Sr_2U_3O_{11}$	Yellow	Triclinic (pseudo-rhombohedral)	6.484 (1)	6.523 (1)	6.484 (1)	35.44(1)	36.10(1)	35.44(1)			9
$SrU_4O_{12.8}$	Light brown	monoclinic (pseudo-orthorhombic)	6.734 (1)	4.193 (1)	4.065 (1)	90	90.16(1)	90			
Sr_2UO_5	Yellow	monoclinic	8.104 3(13)	5.661 4(8)	11.918 5(18)	90	108.985(10)	90	$P2_1/c$	4	13
Sr_3UO_6	Pale yellow	monoclinic	5.958 8(22)	6.179 5(22)	8.553 5(38)	90	90.192 (41)	90	$P2_1$	2	

[a] Numbers in parentheses refer to standard deviations in units of the last decimal place. [b] This work.

The strontium uranate(VI) compounds are hygroscopic, as evidenced by a steady increase in weight from the moment the compound is removed from the furnace. All the measurements were therefore made as quickly as possible, although no appreciable change occurred in the i.r. spectra after exposure of the samples to air for several days.

Infrared Measurements.—Infrared spectra were recorded using a Perkin-Elmer model 225 spectrophotometer. All the measurements were at room temperature and samples were prepared both as Nujol mulls and compressed potassium bromide discs for spectra recorded in the 200—1 000 cm^{-1} region. Since Nujol exhibits an absorption at 730 cm^{-1} it was necessary to use the KBr disc method to examine this part of the spectrum.

Raman Measurements.—Raman spectra for β-$SrUO_4$, $Sr_2U_3O_{11}$, Sr_2UO_5, and Sr_3UO_6 in powder form were obtained from a Coderg T800 spectrometer, with a triple monochromator, using the 647.1-nm krypton line. The other compounds could not be studied due to their dark colour and consequent poor light-scattering properties.

X-*Ray Measurements*.—*X*-Ray powder-diffraction photographs were taken with a Philips PW1011 instrument and Debye–Scherrer camera with Cu-K_α radiation at 1.541 8 Å.

RESULTS AND DISCUSSION

Crystal data presently available for these systems are summarised in Table 1. Since there is some disagreement between the reported colours of some of the strontium uranate(VI) compounds, Table 1 also includes the colour of the compounds prepared during the course of this work. $SrU_4O_{12.8}$ showed some variability in colour; the colour intensified to a darker brown if heating was prolonged. A bright orange colour was obtained from mixtures of β-$SrUO_4$ and $SrU_4O_{12.8}$.

The *X*-ray powder-diffraction patterns obtained for the compounds β-$SrUO_4$, Sr_2UO_5, Sr_3UO_6, $Sr_2U_3O_{11}$, and $SrU_4O_{12.8}$ all agreed with the published data[8,10,12,13] and are therefore not repeated here.

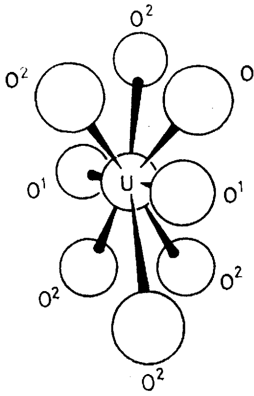

FIGURE 1 Diagrammatic representation of the co-ordination polyhedron surrounding the uranium atom in a typical metal uranate(VI) compound

Infrared and Raman Spectra.—The type of structure commonly found in metal uranate(VI) systems consists of a linear uranyl group with between four and six secondary oxygen atoms arranged in the plane perpendicular to the axis of the UO_2 group (see Figure 1). The uranium(VI) atom thus has a co-ordination number between six and eight. The metal counter ion (in this

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[13] B. O. Loopstra and H. M. Rietveld, *Acta Cryst.*, 1969, **B25**, 787.

case, strontium) usually forms ionic bonds with the secondary oxygen atoms, but may, in some cases, also bond to the primary oxygen atoms.[14,15] The length of the primary U–O^1 bonds varies according to the environment of the uranyl group, so that a compound with very short U–O^1 bonds is closer to containing ' free ' uranyl groups than one in which the difference between the U–O^1 and U–O^2 distances is less pronounced.

Figures 2 and 3 show the i.r. and Raman spectra for the compounds studied. The vibrational frequencies are listed in Tables 2 and 3. Most of the i.r. bands are broad and overlap, particularly in the 300—600 cm^{-1} region where the U–O stretching modes occur. Interpretation of these bands is not easily achieved, but in the portion of the spectrum above 700 cm^{-1} the stretching vibrations of the uranyl group are to be found and it is noteworthy that the compounds β-$SrUO_4$, $Sr_2U_3O_{11}$, and $SrU_4O_{12.8}$ each show several lines above 710 cm^{-1}, whereas for Sr_2UO_5, Sr_3UO_6, and $SrUO_{3.67}$ no such bands can be seen. Weak bands, however, could be concealed by the broad intense absorptions centred at lower frequency.

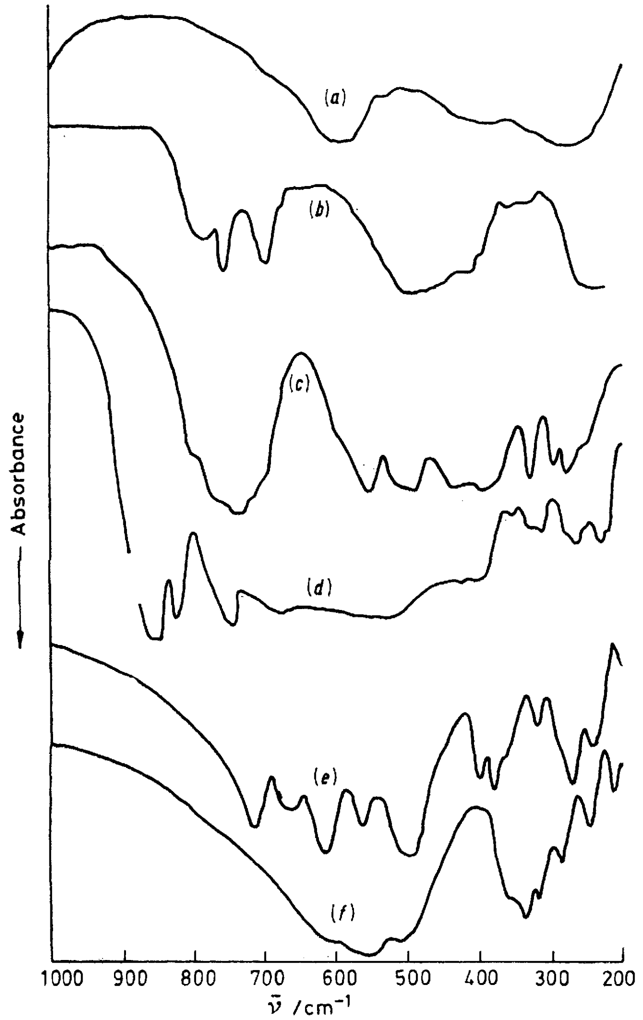

FIGURE 2 Infrared spectra of strontium uranate(VI) compounds: (*a*) $SrUO_{3.67}$, (*b*) β-$SrUO_4$, (*c*) $Sr_2U_3O_{11}$, (*d*) $SrU_4O_{12.8}$, (*e*) Sr_2UO_5, and (*f*) Sr_3UO_6

β-$SrUO_4$, $Sr_2U_3O_{11}$, $SrU_4O_{12.8}$, Sr_2UO_5, and Sr_3UO_6 can be considered as compounds in which the uranium environment is essentially octahedral where one pair of opposite bonds (the axial set) may be shorter than the rest. When these bonds are considerably shorter than the others, the vibrations of the axial set (the ' uranyl ion ') may be considered separately.

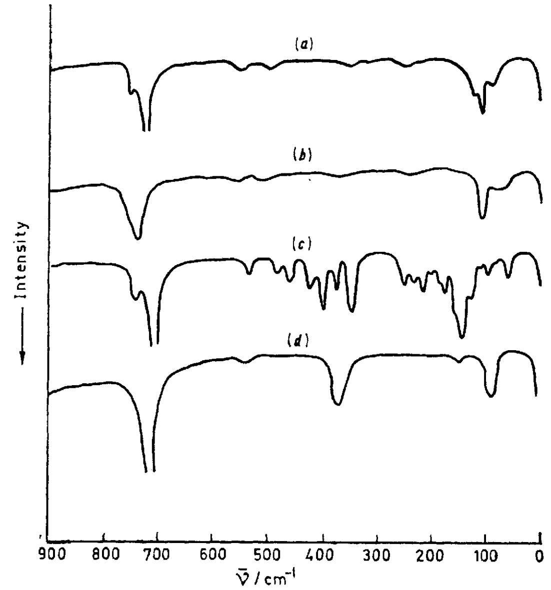

FIGURE 3 Raman spectra of strontium uranate(VI) compounds: (*a*) β-$SrUO_4$, (*b*) $Sr_2U_3O_{11}$, (*c*) Sr_2UO_5, and (*d*) Sr_3UO_6

Group theory predicts three fundamental vibrations for an isolated linear $[UO_2]^{2+}$ ion, with point group $D_{\infty h}$. These are the symmetric (Σ_g^+) and antisymmetric (Σ_u^+) stretching modes, and the two degenerate bending modes (Π_u). Of these, the antisymmetric stretching and the bending modes should be i.r. active, and the symmetric stretching mode Raman active. No coincidences should be observed if the group is centrosymmetric. In a crystalline strontium uranate(VI) compound the U–O distance in the uranyl group will depend on the structure of the crystal lattice in question or more specifically on the symmetry of the site occupied by the U^{VI} atom in

TABLE 2

Infrared bands (cm^{-1}) for strontium uranate(VI) compounds

Compound	
$SrUO_{3.67}$	690 (sh), 600s (br), 530w, 400m (br), 250s (br)
β-$SrUO_4$	785m, 751s, 697s, 490s (br), 415 (sh), 250s (br)
$Sr_2U_3O_{11}$	800 (sh), 770 (sh), 739s (br), 705 (sh), 550s, 425m, 390m, 338s, 292m, 270m, 245 (sh)
$SrU_4O_{12.8}$	853s, 829s, 750s, 680—390br, 338w, 310w, 270m, 235m
Sr_2UO_5	710s, 662m, 620s, 560m, 500s, 398m, 379m, 360 (sh), 325m, 280s, 263m, 242 (sh)
Sr_3UO_6	620 (sh), 550s (br), 505s (br), 352 (sh), 340m, 320m, 285m, 248m, 208m

s = Strong; m = medium; w = weak; sh = shoulder; br = broad.

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[14] B. W. Veal, D. J. Lam, W. T. Carnall, and H. R. Hoekstra, *Phys. Rev.*, 1975, **12**, 5651.

[15] H. R. Hoekstra, *J. Inorg. Nuclear Chem.*, 1965, **27**, 801.

the lattice and the extent to which it is bound to the nearest-neighbour secondary oxygen atoms. As a consequence of such interactions the antisymmetric Σ_u^+ vibration of the uranyl group might show marked variations in frequency in the i.r. spectrum and there may be some activation of the Σ_g^+ mode. Unfortunately, in the absence of detailed information on the site symmetries for these compounds, no precise predictions can be made regarding the numbers of lines seen in the i.r. and Raman spectra.

Each of the Raman spectra which could be obtained (for β-$SrUO_4$, Sr_2UO_5, Sr_3UO_6, and $Sr_2U_3O_{11}$) exhibits a very strong band between 700 and 755 cm^{-1}, and a rather less strong broad band at *ca.* 100 cm^{-1}. In the case of β-$SrUO_4$ and $Sr_2U_3O_{11}$ these are the only bands found. Sr_3UO_6 has a third strong band at 370 cm^{-1}, and Sr_2UO_5 gave a much better resolved spectrum showing 19 lines between 50 and 550 cm^{-1}. The band between 700 and 755 cm^{-1}, from its position and intensity, must be the symmetric stretching vibration of the U–O octahedron and it is interesting to compare this with the corresponding i.r. spectrum in each case.

TABLE 3

Raman bands of strontium uranate(VI) compounds

Compound	
β-$SrUO_4$	755w, 737s, 125w, 114m, 80w
$Sr_2U_3O_{11}$	755s, 110m, 75w
Sr_2UO_5	738w, 708s, 520w, 485w, 455w, 420w, 404m, 385w, 353m, 255w, 242w, 220w, 199w, 180 (sh), 172w, 146 (sh), 140m, 132 (sh), 117w, 98w, 68w
Sr_3UO_6	714s, 368m, 94m

β-$SrUO_4$ has a second Raman line between 700 and 755 cm^{-1}, much less strong than the first. This may arise from a similar vibrational mode, indicating the presence of more than one type of uranium environment in the crystal, or it may be due to excitation of the antisymmetric mode by the site symmetry of the uranium atoms. This line coincides with the strongest line in the i.r. spectrum (755 cm^{-1}), lending support to the latter alternative. The stronger Raman line is at 737 cm^{-1}, and does not correlate with any i.r. line.

$Sr_2U_3O_{11}$ has a broad i.r. absorption in the 'uranyl' region, centred on 740 cm^{-1}. Its Raman spectrum shows a band at 755 cm^{-1}, which lies within the region of the i.r. absorption, but the resolution is insufficient to see any line coincidences. The i.r. spectrum is very similar to those published by Klíma *et al.*[6] who had probably prepared this compound in an impure form.

The Raman line at 714 cm^{-1} for Sr_3UO_6 does not fall near any i.r. absorption, and in this compound the distinction between primary and secondary oxygen atoms is probably meaningless since bond-length information indicates that here the environment of the uranium atoms is much closer to being regular octahedral than in the other strontium uranate(VI) compounds. Although no two bond lengths are the same in Sr_3UO_6, the difference between the shortest and the longest is relatively small.

Sr_2UO_5 shows a strong Raman absorption at 708 cm^{-1}, with a small secondary line at 738 cm^{-1}. From neutron-diffraction experiments Loopstra and Rietveld [13] found that two uranium atoms in this compound have slightly different environments, so this result is not entirely unexpected.

A reasonable estimate of the U–O^1 bond length can be made using relation (1) developed by Veal *et al.*[14] from Badger's Rule,[16,17] where R(U–O^1) is the bond length in

$$R(\text{U–O}^1) = 81.2\nu^{-\frac{2}{3}} + 0.895 \qquad (1)$$

Å and ν is the frequency in cm^{-1} of the antisymmetric stretching vibration of the UO_2 group. The antisymmetric vibration is customarily at higher frequency than the symmetric vibration [15] and therefore, choosing the highest-frequency i.r. line in each case, the following bond lengths (Å) are found:

β-$SrUO_4$	1.85
$Sr_2U_3O_{11}$	1.84
$SrU_4O_{12\cdot8}$	1.79

The U–O^1 bond length in $SrU_4O_{12\cdot8}$ is rather short for a metal uranate(VI) compound, indicating a relatively 'free' uranyl group with strong U–O^1 bonds and somewhat weakened secondary U–O^2 bonds. It may be noted in this connection that this compound decomposes at 1 130 °C, yielding U_3O_8 and $Sr_2U_3O_{11}$.[9] The bonding in $SrU_4O_{12\cdot8}$ is also complicated by the probable presence of U^V, making it unique among the compounds studied (with the possible exception of $SrUO_{3.67}$).

The line at 710 cm^{-1} in the i.r. spectrum of Sr_2UO_5 is almost certainly due to antisymmetric U–O stretching, and application of the bond-length formula gives a result of 1.92 Å. The bonding in this compound is therefore intermediate in type between the situation found in β-$SrUO_4$, $Sr_2U_3O_{11}$, and $SrU_4O_{12\cdot8}$ which contain uranyl groups in a more or less 'free' state, and the more symmetrical uranium environment of Sr_3UO_6, in which the six oxygen atoms form a relatively regular octahedral structure around the uranium atom.

The Compound $SrUO_{3.67}$.—The loss in weight of β-$SrUO_4$ on reduction in hydrogen indicated the formation of a compound with formula $SrUO_{3.67}$. The *X*-ray powder photograph, however, showed two overlapping patterns, both arising from rhombohedral structures, with one pattern rather stronger than the other. The weaker pattern disappeared over a period of a few hours, with no new lines being formed, so the formula $SrUO_{3.67}$ probably represents a weighted average of two oxygen-deficient phases, one of which takes up oxygen at room temperature to form the other. Cordfunke and Loopstra [9] found a similar effect and deduced the approximate compositions $SrUO_{3.3}$ and $SrUO_{3.75}$ for the two phases, but, whereas they found the cell dimensions to be a = 6.64 Å and α = 35.0° and a = 6.58 Å and α = 35.3° respectively, the dimensions found in the

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[16] R. M. Badger, *J. Chem. Phys.*, 1934, **2**, 128.

[17] R. M. Badger, *J. Chem. Phys.*, 1935, **3**, 710.

present work are $a = 6.68$ Å and $\alpha = 35.55°$ for the stronger pattern and $a = 6.35$ Å and $\alpha = 33.1°$ for the weaker one. Since the i.r. spectrum of $SrUO_{3.67}$ shows no bands higher than 650 cm^{-1}, from a consideration of the expression (1), it follows that the substance is unlikely to contain U–O bond lengths shorter than 2.00 Å. This is inconsistent with the structure assigned to α-$SrUO_4$ by Zachariasen[8] which requires linear UO_2 groups with a U–O bond distance of 1.91 Å. Since it was suggested in the introduction that $SrUO_{3.3}$, $SrUO_{3.4}$, $SrUO_{3.67}$, $SrUO_{3.75}$, and α-$SrUO_4$ should be considered as a closely related group, there is cause to question whether the compound studied by Zachariasen is the same as that made by the reduction of β-$SrUO_4$ in hydrogen.

Conclusions.—(1) Heating mixtures of strontium carbonate and U_3O_8 in air between 850 and 1 000 °C for 24 h gives the following compounds: β-$SrUO_4$ (bright yellow), $Sr_2U_3O_{11}$ (yellow), $SrU_4O_{12.8}$ (light brown), and Sr_3UO_6 (pale yellow). Heating a mixture of β-$SrUO_4$ and Sr_3UO_6 gives Sr_2UO_5 (yellow). The *X*-ray powder-diffraction patterns for all these compounds agree with published data.

(2) Reduction of β-$SrUO_4$ in hydrogen at 850 °C gives a dark grey product containing two oxygen-deficient rhombohedral phases with cell constants $a = 6.68$ Å and $\alpha = 33.35$ and $a = 6.35$ Å and $\alpha = 33.1°$, the second of which takes up oxygen at room temperature to form the first. Infrared spectroscopy indicates that no U–O bonds shorter than 2.00 Å are present.

(3) The i.r. spectra of the compounds β-$SrUO_4$, $Sr_2U_3O_{11}$, Sr_2UO_5, $SrU_4O_{12.8}$, and Sr_3UO_6 all show complex patterns between 200 and 1 000 cm^{-1}, any one of which can be used to distinguish that compound from the others.

(4) By application of relation (1) to the frequency of the antisymmetric stretching vibration of the UO_2 group, bond lengths for $SrU_4O_{12.8}$, $Sr_2U_3O_{11}$, β-$SrUO_4$, and Sr_2UO_5 (1.92 Å) can be found (see above). The i.r. spectrum of Sr_3UO_6 shows no lines characteristic of uranyl groups, and therefore the uranium atoms in this compound probably have a fairly symmetrical octahedral environment. The short bond length in $SrU_4O_{12.8}$ suggests a relatively ' free ' uranyl group. β-$SrUO_4$ and $Sr_2U_3O_{11}$ both contain uranyl groups with bond lengths typical of metal uranate systems. Sr_2UO_5 has a structure intermediate between these and the more symmetrical Sr_3UO_6.

(5) The Raman spectra of β-$SrUO_4$, $Sr_2U_3O_{11}$, Sr_2UO_5, and Sr_3UO_6 all contain a strong line between 700 and 750 cm^{-1}, attributable to the symmetric stretching vibration of U–O bonds.

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