Vibrational Spectroscopy of Alkaline-earth Metal Uranate Compounds

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Solid-state reactions have been used to prepare $MgUO_{4-x}$ (*x ca.* 0.05), $MgU_3O_{8.9}$, $CaUO_{4-x}$ (*x ca.* 0.20), Ca_2UO_5, Ca_3UO_6, $Ca_2U_3O_{11}$, CaU_2O_7, CaU_4O_{12}, $BaUO_4$, Ba_3UO_6, BaU_2O_7, $Ba_2U_2O_7$, and $Ba_2O_3O_{11}$. These compounds have been characterised using i.r. and Raman spectroscopy together with *X*-ray powder diffraction. The spectra are presented and discussed and the length of the shortest uranium–oxygen bond in many cases calculated from the frequency of its antisymmetric stretching vibration.

VIBRATIONAL spectra of some uranium oxides and strontium uranates have already been reported.[1,2] The present paper extends the range of the study of strontium uranate compounds to below 100 cm^{-1} and includes the uranate compounds of magnesium, calcium, and barium. Published vibrational data on the alkaline-earth metal uranates is very incomplete, many of these compounds never having been studied from a spectroscopic viewpoint. However, the literature is not completely devoid of information. A number of workers have published results on some compounds of this type.[3-8]

Here we continue to use the approach which we applied earlier to the strontium uranates.[2] Thus the environment of the uranium ion is regarded as a more or less distorted polyhedron of oxygen ions. The distortion is encouraged by the strong tendency of U^{VI} to form a linear uranyl ion $[U^{VI}O_2]^{2+}$, whereby two uranium–oxygen bonds (the 'primary', or U-O^1, bonds) are shorter and stronger than the 'secondary', or U-O^2, bonds, of which there are four or six. There is, however, no firm dividing line between compounds that do and do not contain uranyl groups. The value of i.r. and Raman spectra in this connection lies in the fact that the vibrations of the U–O^1 bonds can in many cases be distinguished from those of the U–O^2 bonds, and the degree of distortion of the UO_6 or UO_8 polyhedron can be seen. In those cases where the antisymmetric stretching vibration of the primary uranium–oxygen

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

bonds can be identified, the relation (1), derived by Veal *et al.*,[9] has been applied to obtain the U–O^1 bond length, where *R* is the bond length in Å and ν is the wavenumber in cm^{-1}. The influence of the secondary U-O bonds should not be wholly disregarded even in those compounds which contain a relatively free uranyl group, but the equation has been shown to represent a good empirical relation for U-O bond lengths ranging from <1.7 to nearly 2.1 Å in 18 different compounds, including many solid uranates.[9] It is our belief that the errors introduced by neglecting secondary bond interactions are small enough to render the calculation worthwhile in this case.

TABLE 1

Methods used to prepare alkaline-earth metal uranate compounds

Compound	Starting materials	Reaction conditions	Colour
$BaUO_4$	$Ba[CO_3],U_3O_8$	24 h in air at 850 °C	Yellow
Ba_3UO_6	$Ba[CO_3],U_3O_8$	36 h in air at 900 °C	Yellow
BaU_2O_7	Acetates of Ba and U	24 h in air at 640 °C	Yellow-brown
$Ba_2U_2O_7$	$BaUO_4$	1 h in flowing H_2 at 750 °C	Grey-brown
$Ba_2U_3O_{11}$	Acetates of Ba and U	20 h in air at 950 °C	Orange
$CaUO_{4-x}$	$Ca[CO_3],U_3O_8$	5 h in air at 980 °C	Green-ochre
Ca_2UO_5	Acetates of Ca and U	3 h in air at 1 000 °C	Pale yellow
Ca_3UO_6	$Ca[CO_3],U_3O_8$	3 d in air at 1 000 °C	Very pale yellow
$Ca_2U_3O_{11}$	$Ca[CO_3],U_3O_8$	20 h at 700 °C in air, then 3 d at 950 °C	Yellow-ochre
CaU_2O_7	Acetates of Ca and U	48 h in air at 1 100 °C	Light brown
CaU_4O_{12}	$Ca[CO]_3,U_3O_8$	24 h in air at 1 000 °C	Dark brown
$MgUO_{4-x}$	MgO,U_3O_8	8 h in air at 980 °C	Yellow
$MgU_3O_{8.9}$	MgO,U_3O_8	48 h in air at 1 000 °C	Yellow

EXPERIMENTAL

The methods of preparation of the magnesium, calcium, and barium compounds are listed in Table 1. Details of the preparation of the strontium compounds have already been published.[2] The starting materials were all AnalaR grade, except for commercial UO_2, the oxygen content of which had been previously measured as $UO_{2.18}$. This was used to prepare U_3O_8 by heating in air at 1 000 °C for 24 h, after which an *X*-ray diffraction pattern was recorded to check that UO_2 was no longer present. Several of the compounds were prepared by the following 'acetate' method. Uranyl acetate and the appropriate metal carbonate were dissolved together in suitable proportions in acetic acid (glacial acid + 10% water). The mixture was carefully evaporated to dryness, and the resulting solid ground and warmed to decompose the acetates to oxides. High-temperature treatment was then applied, with the compound contained in a silica boat in an electrical resistance furnace.

X-Ray diffraction, i.r., and Raman measurements were obtained as described previously,[2] with the addition that far-i.r. spectra were recorded using a Perkin-Elmer model 180 spectrophotometer, which extends the range of measurement to <100 cm^{-1}.

RESULTS

All the compounds were identified by means of their X-ray diffraction patterns, and their oxygen content was determined, where possible, from the change in weight during preparation. The observed colour for each compound is included in Table 1. The i.r. and Raman spectra are shown in Figures 1—3, and the recorded band positions are listed in Tables 3 and 4.

DISCUSSION

The preparation and study of metal uranates is often complicated by the difficulty in obtaining pure samples. Coexistent phases are frequently encountered and many of the compounds are inclined to be non-stoicheiometric. It was not possible, for instance, to prepare a pure sample of $Ca_2U_3O_{11}$ free from CaU_4O_{12} and $CaUO_4$, despite prolonged heating and repeated grinding, so the spectra of this compound are not reproduced here. The compounds found definitely to contain less oxygen than would be compatible with a uranium(VI) formulation are as follows (strontium compounds are included in the list for comparison): $MgUO_{4-x}$ and $CaUO_{4-x}$ ($x = ca.$ 0.05 and 0.20 respectively), $MgU_3O_{8.9}$, CaU_4O_{12}, $SrUO_{3.67}$, $SrU_4O_{12.8}$, and $Ba_2U_2O_7$. The evidence for the stoicheiometry of the compounds $Ca_2U_3O_{11}$, $Ba_2U_3O_{11}$, and CaU_2O_7 is not decisive, but the compounds $SrUO_4$, Sr_2UO_5, Sr_3UO_6, $BaUO_4$, Ba_3UO_6, BaU_2O_7, $Sr_2U_3O_{11}$, Ca_2UO_5, and Ca_3UO_6 show only slight, if any, deviations from the uranium(VI) formulation. The evidence for this comes from two sources: careful weight measurements before and after the heat treatment (all the compounds were allowed to equilibrate in air at room temperature for $\geqslant 1$ h before the final weighing), and e.s.r. spectra.[10] In every case where an oxygen deficiency was found by weight measurements, the e.s.r. spectrum shows an absorption centred at a $g_{\text{eff.}}$ value of $ca.$ 2.3 ± 0.3, which may be interpreted as arising from the unpaired $5f$ electron associated with a uranium(V) ion.

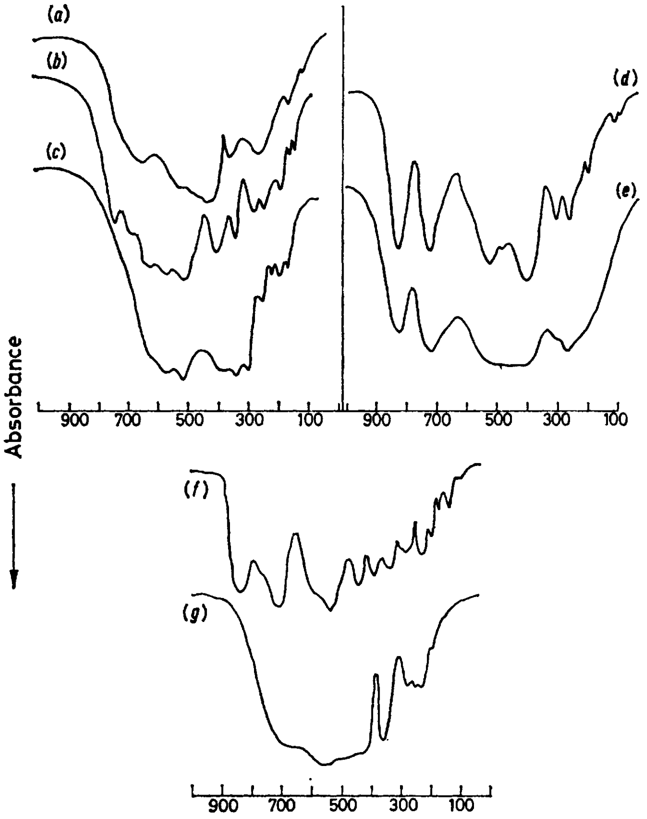

FIGURE 1 Infrared spectra of magnesium and calcium uranate(VI) compounds: (a) $CaUO_{4-x}$, (b) Ca_2UO_5, (c) Ca_3UO_6, (d) CaU_2O_7, (e) CaU_4O_{12}, (f) $MgU_3O_{8.9}$, and (g) $MgUO_{4-x}$

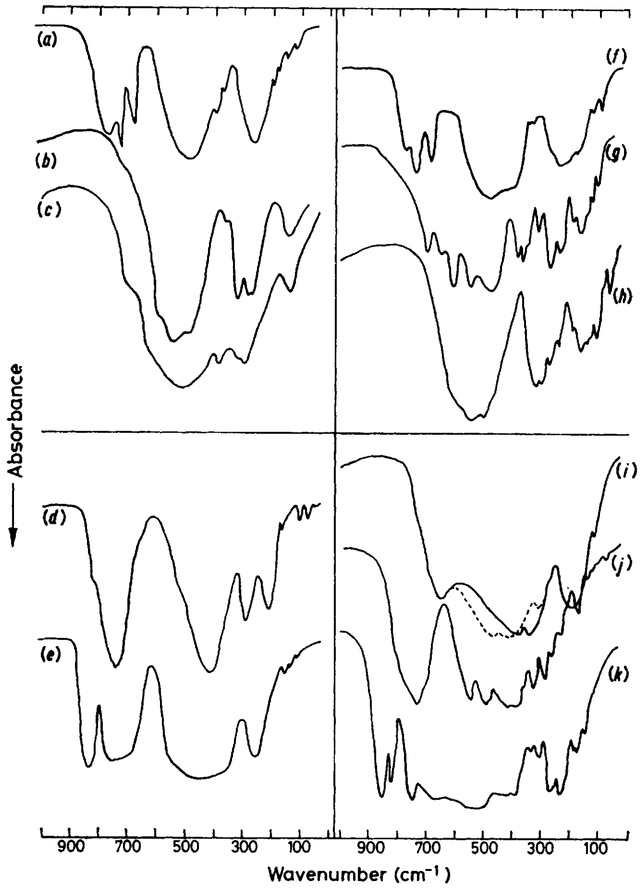

FIGURE 2 Infrared spectra of strontium and barium uranate(VI) compounds: (a) $BaUO_4$, (b) Ba_3UO_6, (c) $Ba_2U_2O_7$, (d) BaU_2O_7, (e) $Ba_2U_3O_{11}$, (f) $SrUO_4$, (g) Sr_2UO_5, (h) Sr_3UO_6, (i) $SrUO_{3.67}$, (j) $Sr_2U_3O_{11}$, and (k) $SrU_4O_{12.8}$

Of the published i.r. spectra of Group 2A uranates, not many are entirely consistent with those reported here. The spectra obtained by Allpress[5] do agree, but only extend to 600 cm⁻¹ and contamination is evident in the spectra of Klima *et al.*[4] and Jakes *et al.*[7] (note the band at 854 cm⁻¹ in $CaUO_4$ and that at 840 cm⁻¹ in Ca_3UO_6). A band at *ca.* 720 cm⁻¹ arising from the Nujol mulling agent has unfortunately been included by Caillet and Brochu[3] in their spectral assignments for the MUO_4 series of compounds.

Examination of the i.r. spectra in Figures 1 and 2 reveals several regions of broad similarity. It will be seen, for example, that Ca_2UO_5 and Sr_2UO_5 have very similar spectra, as do $SrUO_4$ and $BaUO_4$. These two pairs of compounds are known to be isomorphic.[11,12] The spectra of the M_3UO_6 compounds (M = Ca, Sr, or Ba) differ chiefly in the spreading out of bands to lower frequency as the size of the metal ion increases. The first two compounds are known to be isomorphic,[12] but Ba_3UO_6 although in some ways similar in structure has two bands in the ν_1 region of the Raman spectrum (also observed by Kemmler-Sack and Seemann[8]). An explanation of this feature of the Ba_3UO_6 Raman spectrum assumes that the perovskite structure contains uranium in two different octahedral sites, each of which gives rise to an A_{1g} vibration.[13]

Two peaks of equal intensity also appear in the ν_1 region of the Raman spectrum of Ca_2UO_5, a feature which curiously is not observed in the Sr_2UO_5 spectrum, although these compounds are isomorphic and their i.r. spectra closely similar.

The similarity between these results and those of Kemmler-Sack is intriguing. The Raman line at 725 cm^{-1} in the spectrum of Ca_2UO_5 does not coincide with any i.r. absorption. However, a band at 695 cm^{-1} is present in the i.r. spectrum and it is possible that this is visible in the Raman spectrum also, in which case the selection rule could have been lifted by a lowering of the symmetry of the uranium co-ordination sphere and loss of its centre of symmetry. Nevertheless, it is difficult to see how the structure of the calcium compound could be so different from its strontium counterpart that two bands appear instead of one. The band at 696 cm^{-1} could be a consequence of $CaUO_4$ impurity but this is not evident from the i.r. spectrum or the X-ray diffraction pattern. It is possible that the uranium is present in two different sites here also, but perhaps this is a further example in which the presence of an impurity is emphasised in the Raman spectrum.

In several cases during the present study the Raman spectrum was found to be a sensitive monitor of contamination by other uranates. $MgUO_{3\cdot95}$, for example, gave a good Raman spectrum with strong bands at 747, 525, and 277 cm^{-1}. The highest of these is likely to be the A_{1g} symmetric stretching vibration of the uranium co-ordination sphere. There is no line at this wavenumber in the i.r. spectrum. For MgU_3O_9, the Raman spectrum was much less strong but bands at 751, 527, and 277 cm^{-1} are visible, confirming the presence of some $MgUO_{4-x}$.

A further comparison may be drawn between the i.r. spectra of the four compounds $MgUO_{4-x}$, $SrUO_{3\cdot67}$, and $Ba_2U_2O_7$. All four contain a high percentage of U^V, and have a very broad, poorly resolved, absorption region extending up to *ca.* 700 cm^{-1}.

Compounds which have a highly distorted UO_n polyhedron exhibit between one and three, often well resolved, bands at wavenumbers above 700 cm^{-1}. Coupling between these bands and the corresponding stretching modes of the set of secondary U–O bonds, which absorb at *ca.* 500 cm^{-1}, is at a minimum for these compounds. In Table 2 the positions of the absorptions due to the symmetric (ν_1) and antisymmetric (ν_3) stretching vibrations of the primary U–O bonds in the Raman and i.r. spectra respectively are listed for those compounds which have such distorted polyhedra. The identification of the ν_1 line is in most cases not difficult, since it is the only strong absorption in the region of the Raman spectrum above 600 cm^{-1}. Unfortunately, the Raman spectra of several compounds could not be measured due to their dark colour, and no figure for ν_1 is entered in Table 2 in such cases. The complete assignment of the i.r. spectrum is extremely difficult in most cases due to the large number of overlapping bands, and will not be attempted here, but the choice of the ν_3 absorption is aided by the fact that it customarily appears as the vibration with the highest frequency in the i.r. spectrum.

TABLE 2

Bond lengths and force constants calculated for some Group 2A uranates

	Wavenumber (cm^{-1})		U–O¹ bond length	Force constant ($\times 10^{-19}$ N cm^{-1})	
Compound	ν_1	ν_3	(Å)	a_{11}	a_{12}
$MgU_3O_{8\cdot9}$	751	840	1.81	6.26	−0.31
CaU_2O_7		835	1.81		
CaU_4O_{12}		825	1.82		
$SrUO_4$	737	785	1.85	6.12	0.39
$Sr_2U_3O_{11}$	755	810	1.83	6.07	−0.044
$SrU_4O_{12\cdot8}$		853	1.79		
$BaUO_4$	726	765	1.87	5.51	0.059
$Ba_2U_3O_{11}$	739	830	1.81	6.09	−0.32
BaU_2O_7	745	740	1.89	5.52	0.35

The bond lengths calculated from ν_3 are included in Table 2, together with the stretching force constants of the $U–O^1$ bonds, which have been calculated from ν_1 and ν_3 using the formulae for the normal vibrations of a linear XY_2 molecule.[14] The bending force constant a_{33} has not been calculated due to the difficulty in identifying the ν_2 vibration in the i.r. spectra. It will be seen that the magnitude of the interaction force constant, a_{12}, is in no case more than 5% of the stretching force constant and takes both positive and negative values. If a_{12} were neglected in the calculation, for example when ν_3 or ν_1 alone is used to calculate a_{11}, then an error of *ca.* 5% would be introduced. An approximate value of ν_1 can be derived for those cases where it has not been possible to measure it, by taking $a_{12} = 0$ and a_{11} as the figure calculated from ν_3. This gives for $SrU_4O_{12\cdot8}$, for example, $a_{11} = 6.726 \times 10^{-19}$ N m^{-1} and ν_1 at 801 cm^{-1}. This value for ν_1 is higher than any of the other measured values. In the absence of a Raman spectrum for this compound, however, the figure must remain unchecked. The high negative values of the interaction force constants for $MgU_3O_{8\cdot9}$ and $Ba_2U_3O_{11}$ are rather surprising. This may indicate incorrect assignment of vibrational lines in these cases.

The calculated bond lengths lie between 1.79 and 1.89 Å, and are in the middle of the range studied by Veal *et al.*[9] The shortest value (1.79 Å), determined for

$SrU_4O_{12 \cdot 8}$, approaches the values found in uranyl salts. This supports an apparent tendency for highly distorted polyhedra with particularly short bonds to be associated with a high proportion of uranium in the compound.

TABLE 3

Observed i.r. bands (cm^{-1}) for Group 2A uranates

Compound		
$MgUO_{4-x}$		700s,br(sh), 535s,br, 465m, 420m(sh), 365s, 282m, 250m, 228m, 197w, 151w
$MgU_3O_{8.9}$		840s, 780m(sh), 715s, 610m(sh), 545s, 450m, 396m, 351m, 315w(sh), 290m, 274w(sh), 240m, 211w, 182w, 148w, 112w
$CaUO_{4-x}$		640s,br, 525s,br, 425br, 360m,br, 270m,br, 165w, 120w
Ca_2UO_5		736m, 695m(sh), 635s, 573s, 511s, 402s, 340m, 274m, 246m, 190w, 161w, 149w
Ca_3UO_6		625m(sh), 565m,br, 520s, 375m, 340m, 306m, 251m, 222w, 192w, 166w
CaU_2O_7		835s, 730s, 615w(sh), 530s, 490w, 410s, 315m, 272m, 240w(sh), 210w, 124w, 104w
CaU_4O_{12}		825s,br, 722,br, 470s,vbr, 302w, 278m, 202m(sh)
$SrUO_4$		785m, 751s, 697s, 490s,br, 415m(sh), 258s,br, 140w, 118w
$SrUO_{3.67}$	L.B.	660s,br, 385s,br, 350s,br, 208s,br, 126w
	D.B.	660s,br, 475s,br, 420s,br, 320m, 208s,br, 126w
Sr_2UO_5		709s, 662w, 620s, 560s, 500s,br, 395m, 378m, 360w(sh), 325m, 279s, 254w, 240w(sh), 203w, 174m, 157w(sh), 139w, 122w
Sr_3UO_6		620m(sh), 550s,br, 505s, 360w(sh), 331m, 315w, 278w, 244w, 202w, 175m, 150w, 141w(sh), 124m, 101w(sh), 77m
$Sr_2U_3O_{11}$		810w(sh), 780w(sh), 739s, 700w(sh), 550s, 500s, 455(sh), 425m, 390m, 338m, 292m, 270w, 230w, 180m, 147w, 85w
$SrU_4O_{12.8}$		853s, 829s, 750s, 675s,br, 525s,br, 430m,br, 395m, 338w, 310w, 270m, 235m, 215w(sh), 193w, 180w, 155w
$BaUO_4$		765s,br, 727s, 682s, 485s,br, 395w, 370w, 265s,br, 204w, 180w, 150w, 131w, 100w
$Ba_2U_2O_7$		710m(sh), 515s,vbr, 390m, 320w(sh), 300m, 145m,br
Ba_3UO_6		715(sh), 685w(sh), 600m(sh), 540s,br, 490m(sh), 365w, 324m, 286w, 270w, 149m,br
$Ba_2U_3O_{11}$		830s,br, 750s,br, 680m(sh), 440s,vbr, 250s,br, 152w, 132w, 110w
BaU_2O_7		825w(sh), 740s,br, 665w(sh), 520w(sh), 420s,br, 294m, 215m, 168w, 103w, 78w, 61w

s = Strong, m = medium, w = weak, sh = shoulder, br = broad, L.B. = light brown compound, D.B. = dark brown compound.

An improvement over previous spectral measurements has been achieved for $SrUO_{3.67}$. This compound, made here by the reduction of $SrUO_4$ in a stream of hydrogen at 750—850 °C, consists, immediately after preparation, of a mixture of two phases, one light brown and one dark brown. The darker phase appears to oxidise on exposure to air, forming the lighter one which is stable. Figure 2 shows i.r. spectra for both phases and here the broken line corresponds to the darker one. The highest peak, at 660 cm^{-1}, is common to both, and according to the bond-length relation this band corresponds to a U–O^1 distance of 1.97 Å. The value obtained by this method is higher than that determined by Zachariasen from X-ray diffraction measurements on 'α-$SrUO_4$', the structure of which requires linear uranyl groups with a U–O bond length of 1.91 Å.[15] However, it is highly probable that α-$SrUO_4$ is in reality an oxygen-deficient form of $SrUO_4$ and not a true polymorph.[4]

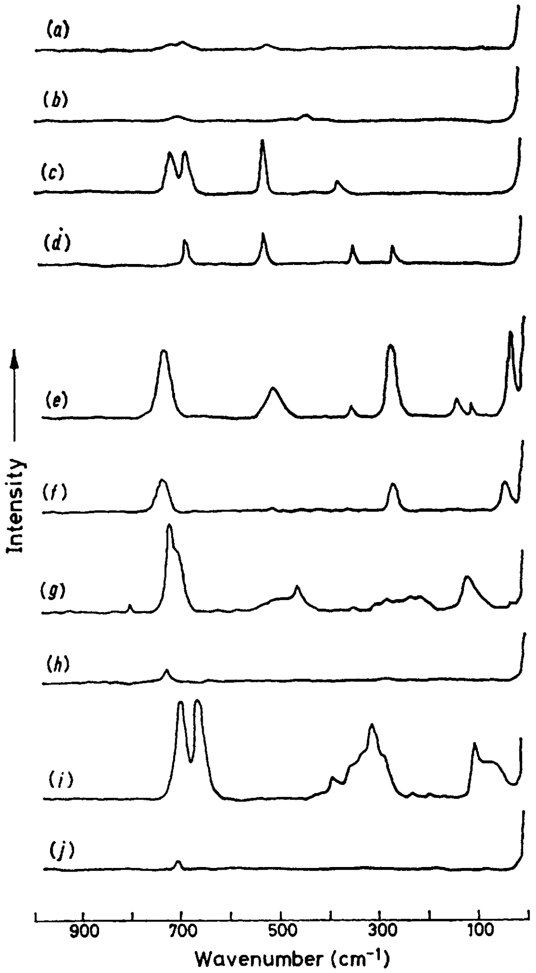

FIGURE 3 Raman spectra of some alkaline-earth metal uranate(VI) compounds: (*a*) Ca_3UO_6, (*b*) CaU_2O_7, (*c*) Ca_2UO_5, (*d*) $CaUO_4$, (*e*) $MgUO_{4-x}$, (*f*) $MgU_3O_{8.9}$, (*g*) $Ba_2U_3O_{11}$, (*h*) BaU_2O_7, (*i*) (*i*) Ba_3UO_6, and (*j*) $BaUO_4$

TABLE 4

Observed Raman bands (cm^{-1}) for Group 2A uranates

Compound	
$SrUO_4$	755w, *737s*, 125w, 114m, 80w
Sr_2UO_5	738w, *708s*, 520w, 485w, 455w, 420w, 404m, 385w, 353m, 255w, 242w, 220w, 199w, 180w(sh), 172w, 146w(sh), 140m, 132w(sh), 117w, 98w, 68w
Sr_3UO_6	*714s*, 368m, 94m
$Sr_2U_3O_{11}$	*755s*, 110m, 75w
$MgUO_{4-x}$	*747s*, 525m, 360w, 277s, 141w, 110w, 35m
$MgU_3O_{8.9}$	*751s*, 746w(sh), 527w, 363w, 330w, 277m, 40m
$CaUO_{4-x}$	*695m*, 533m, 351w, 267w
Ca_2UO_5	*725m*, *696m*, 535m, 379w
$BaUO_4$	*726w*
Ba_3UO_6	*721s*, *685s*, 436w, 401w, 365w(sh), 340w(sh), 320m, 295w, 232w, 198w, 106m, 58m
BaU_2O_7	*745w*
$Ba_2U_3O_{11}$	817w, *739*s, 727w(sh), 477m,br, 358w, 316w(sh) 283w, 236w, 218w, 122m, 36w, 30w

Italicised value considered to be due to totally symmetric A_{1g} vibrations.

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