# Analysis of the Luminescence Spectra of some Uranates

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In this paper the luminescence spectra of $Y_6UO_{12}$, $Li_4UO_5$, $Li_2UO_4$, and $MgUO_4$ are discussed. Emission and excitation spectra and the decay time of the luminescence have been measured at low temperatures ($T < 10$ K). The vibrational structure which is observed in the emission spectra of the investigated uranates is analysed. The electronic transitions observed in the excitation spectra are assigned to charge-transfer transitions within the intrinsic uranate groups.

In the past few years the luminescence properties of uranate centres in solids have been studied extensively in our laboratory (see *e.g.* refs. 1—4). The greater part of the investigations have been performed on oxides, containing small amounts (<1 mole %) of hexavalent uranium as a dopant. The uranate luminescence of these diluted systems appears to be very sensitive to crystal structure and chemical composition (see *e.g.* refs. 1 and 2). This manifests itself in the quenching temperature and the decay time of the luminescence and in the vibrational structure, which is observed in the luminescence spectra.

Recently, the excitation spectra of the luminescence of $UO_6^{6-}$ groups in various compounds have been analysed.[5] The excitation bands were assigned to different charge-transfer transitions within the uranate groups. The assignments were based on experimental and theoretical work on $UF_6$,[6-8] which is isoelectronic with the $UO_6^{6-}$ group.

In a previous paper [9] we reported on the energy-transfer processes in uranates. In these concentrated uranium compounds the luminescence properties are determined by the occurrence of energy migration, even at low temperatures. After excitation in the intrinsic uranate groups, the energy migrates through the lattice till it is trapped at uranate centres near defects (traps), which have slightly different energy levels. It is from these traps that the luminescence originates.

In this work we will try to assign the features which are observed in the luminescence spectra of these uranates to electronic and vibronic transitions within the uranate groups. As far as the emission spectra are concerned, attention will be paid mainly to the vibrational structure in these spectra. In the case of the excitation spectra we will concentrate on the electronic transitions which are involved in the excitation processes.

The investigated compounds are $Ba_2CaUO_6$, $Y_6UO_{12}$, $Li_4UO_5$, $Li_2UO_4$, and $MgUO_4$. The luminescence properties of $Ba_2CaUO_6$ and $MgUO_4$ have already been reported in refs. 10 and 11, respectively. For these compounds some additional results are presented here.

In view of the crystal structures, which have been described before,[9,10] the luminescence spectra of the investigated uranates will be discussed taking the uranate octahedron as a starting point. The site symmetry of the $U^{6+}$ ion is $S_6$ in $Y_6UO_{12}$,[12] $C_{4h}$ in $Li_4UO_5$,[13] $C_s$ in $Li_2UO_4$,[14] and $C_{2v}$ in $MgUO_4$.[15] The crystal structure of $Ba_2CaUO_6$ is not exactly known, but the site symmetry of the $U^{6+}$ ion in this compound will be close to $O_h$.

In this paper the assignments in the emission and excitation spectra of the above-mentioned uranates are discussed.

## EXPERIMENTAL

The preparation of the uranate powders has been described before.[9-11] The set-up for the luminescence measurements has already been described in ref. 9. For the performance of the excitation spectra over a wide spectral region ($250 < \lambda_{exc.} < 550$ nm) a Perkin-Elmer MPF 2A spectrofluorimeter was used. In this case low temperatures were obtained by mounting the sample in an Oxford CF 100 continuous flow helium cryostat. The excitation spectra were corrected for the lamp intensity and the transmittance of the monochromator with the use of Lumogen T-Rot GG as a standard.[16] The set-up for the decay measurements has been described in ref. 17. As an excitation source a Xe flash lamp with a pulse width of a few microseconds was used.

The i.r. spectra of $Y_6UO_{12}$ and $Li_2UO_4$ were measured on CsI discs. For the performance of the Raman spectra of $Y_6UO_{12}$, $Li_4UO_5$, and $MgUO_4$ the samples were excited with the 488 nm line of an $Ar^+$ laser. In the case of $Li_2UO_4$ the 647 nm line of a $Kr^+$ laser was used.

## RESULTS

The emission spectra of $Y_6UO_{12}$, $Li_4UO_5$, $Li_2UO_4$, and $MgUO_4$, recorded at low temperatures, are presented in Figures 1—4. The features which have been observed in these spectra have been listed in Tables 1—4.

The vibrational data, which were obtained by measuring the i.r. and Raman spectra of the uranates, are also listed in these Tables.

The excitation spectra of the luminescence of $Ba_2CaUO_6$, $(Y_{0.99}Eu_{0.01})_6UO_{12}$, and $Li_4UO_5$, measured at 4.2 K, are shown in Figure 5(*a*)—5(*c*). In the case of $Y_6UO_{12}$ the uranate emission was so weak that it was not possible to measure an excitation spectrum. The uranate excitation spectrum was obtained by monitoring the $Eu^{3+}$ luminescence of $(Y_{0.99}Eu_{0.01})_6UO_{12}$. The spectra which are presented in Figure 5(*a*)—5(*c*) consist of several excitation bands, some of which show vibrational structure. The positions of these different bands have been listed in Table 5. For the structured bands the position is indicated by the energy of the electronic origin. For the broad unstructured bands the position is indicated by the energy of the maximum of

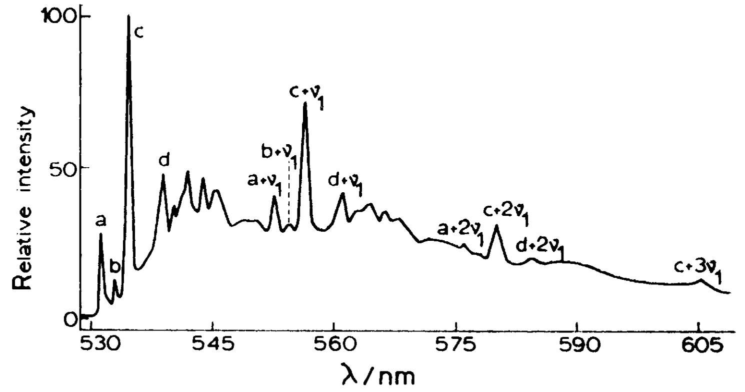

FIGURE 1 Emission spectrum of $Y_6UO_{12}$, recorded at 1.4 K. The excitation wavelength is *ca.* 400 nm. For the explanation of the symbols see Table 1 and text

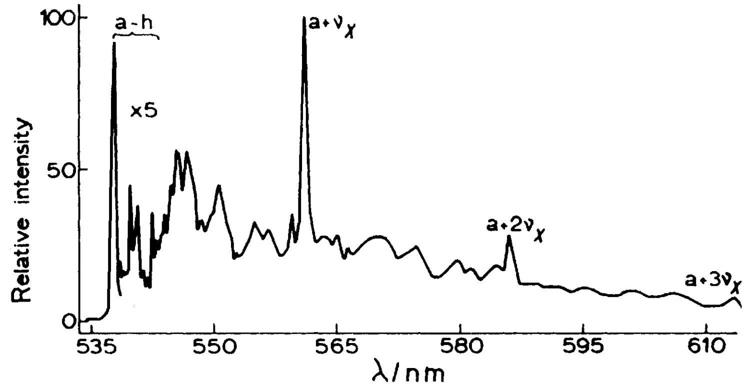

FIGURE 2 Emission spectrum of $Li_4UO_5$, recorded at 4.2 K. The excitation wavelength is *ca.* 400 nm. For the explanation of the symbols see Table 2 and text

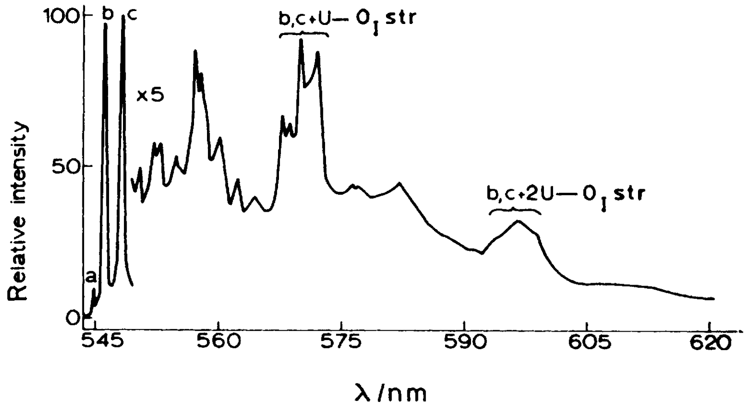

FIGURE 3 Emission spectrum of $Li_2UO_4$, recorded at 4.2 K. The excitation wavelength is *ca.* 400 nm. For the explanation of the symbols see Table 3 and text

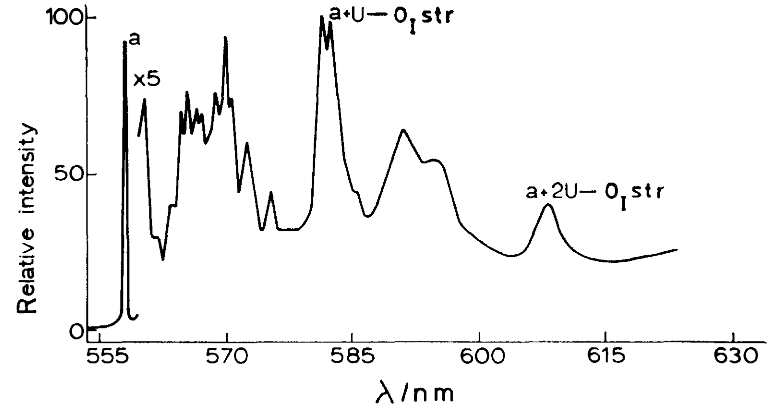

FIGURE 4 Emission spectrum of $MgUO_4$, recorded at 8 K. The excitation wavelength is *ca.* 400 nm. For the explanation of the symbols see Table 4 and text

the band (see also ref. 5). Note that for $Y_6UO_{12}$ the electronic origin of the first excitation band is split into two components.

In the case of $Li_2UO_4$ and $MgUO_4$ the excitation spectrum consists of a very broad band. This band extends from *ca.* 550 nm into the u.v. region and shows some structure in the long wavelength part of the spectrum. The positions of the sharp lines which are observed in this spectral region have been listed in Table 6.

For $Li_4UO_5$, $Li_2UO_4$, and $MgUO_4$ the decay time of the emission was measured at 4.2 K. The decay curves did not show a single-exponential behaviour. The decay times derived from the tail of the decay curves were 350 μs for $Li_4UO_5$, 130 μs for $Li_2UO_4$, and 100 μs for $MgUO_4$. The decay time of the emission of $Y_6UO_{12}$ could not be measured because of the low emission intensity.

TABLE 1

Assignment of the vibrational structure in the emission of $Y_6UO_{12}$

| λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ [a] | Assignment [b] | Vibr. freq./ cm$^{-1}$ [c] | Assignment [b] |
|---|---|---|---|---|
| 531.2 | 0 | a | i.r. 230m | $\nu_6$, $\nu_4$ |
| 532.8 | 56 | b | i.r. 275m | |
| 534.6 | 119 | c | i.r. 310(sh, w) | |
| 538.8 | 265 | d | R 330(w) | |
| | | | i.r. 350(s) | ‘ Y–O |
| 540.2 | a + 313 | a + $\nu_4$ | R 365(w) | |
| 542.0 | c + 256 | c + $\nu_6$ | i.r. 373(s) | $\nu_4'$ |
| 543.9 | c + 320 | c + $\nu_4$ | i.r. 425(br, s) | ‘ Y–O ’ |
| 545.6 | c + 378 | c + $\nu_4'$ | i.r. 500(w) | $\nu_3$ |
| 549.5(br) | c + 508 | c + $\nu_3$ | R 500(w) | |
| | | | i.r. 530(s) | $\nu_3'$ |
| 552.7 | a + 732 | a + $\nu_1$ | i.r. 580(s) | ‘ Y–O ’ |
| 554.6 | b + 738 | b + $\nu_1$ | R 735(s) | $\nu_1$ |
| 556.4 | c + 733 | c + $\nu_1$ | | |
| 561.0 | d + 735 | d + $\nu_1$ | | |
| 563.0 | a + 1 051 | a + $\nu_1$ + $\nu_4$ | | |
| 564.6 | c + 994 | c + $\nu_1$ + $\nu_6$ | | |
| 566.5 | c + 1 054 | c + $\nu_1$ + $\nu_4$ | | |
| 568.3 | c + 1 110 | c + $\nu_1$ + $\nu_4'$ | | |
| 576.2 | a + 1 470 | a + 2$\nu_1$ | | |
| 580.2 | c + 1 471 | c + 2$\nu_1$ | | |
| 584.8 | d + 1 460 | d + 2$\nu_1$ | | |
| 605.5 | c + 2 191 | c + 3$\nu_1$ | | |

[a] The energy difference is given with respect to the electronic origin to which the vibronic feature belongs; see also text. [b] ‘ Y–O ’ denotes vibrations with mainly Y–O character. The symbols $\nu_1$, $\nu_3$, $\nu_3'$, $\nu_4$, $\nu_4'$, $\nu_6$ refer to vibrations with mainly U–O character; the notation is analogous to the notation for an octahedral complex; see also text. [c] br = Broad, sh = shoulder, w = weak, m = medium, and s = strong; R = observed in the Raman spectrum and i.r. = observed in the infrared spectrum.

TABLE 2

Assignment of the vibrational structure in the emission of $Li_4UO_5$

| λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ [a] | Assignment [b] | Vibr. freq./ cm$^{-1}$ [c] | Assignment [b] |
|---|---|---|---|---|
| 537.7 | 0 | a | R 235(w) | $\nu_7(E_g)$ |
| 539.3 | 55 | b | i.r. 292 | $\nu_3(A_{2u})$ |
| 539.5 | 62 | c | i.r. 333 | $\nu_9(E_u)$ |
| 539.8 | 73 | d | R 345(w) | |
| 540.4 | 93 | e | i.r. 430 | $\nu_2(A_{2u})$ |
| 540.7 | a + 103 | a + $\nu_l$ | R 435(w) | $\nu_5(B_{2g})$ |
| 541.5 | 131 | f | R 520(m) | $\nu_4(B_{1g})$ |
| 541.9 | 144 | g | i.r. 590(s, br) | $\nu_8(E_u)$ |
| 542.5 | 165 | h | R 720(s) | $\nu_1(A_{1g})$ |
| 543.0 | a + 182 | | | |
| 543.6 | a + 202 | | | |
| 544.0 | a + 216 | | | |
| 544.8 | a + 243 | | | |
| 545.4 | a + 263 | | | |
| 545.6 | a + 270 | | | |
| 546.6 | a + 303 | | | |
| 548.5 | a + 366 | | | |
| 549.7 | a + 406 | | | |
| 550.6 | a + 436 | | | |
| 552.7 | a + 505 | | | |
| 554.7 | a + 570 | | | |
| 556.5 | a + 628 | | | |
| 559.4 | a + 722 | a + $\nu_1$ | | |
| 561.0 | a + 773 | a + $\nu_x$ | | |
| 563.7 | a + 858 | | | |
| 565.0 | a + 899 | | | |
| 565.2 | a + 905 | | | |
| 566.3 | h + 774 | h + $\nu_x$ | | |
| 584.6 | a + 1 492 | a + $\nu_x$ + $\nu_1$ | | |
| 586.2 | a + 1 539 | a + 2$\nu_x$ | | |
| 613.5 | a + 2 298 | a + 3$\nu_x$ | | |

[a] See Table 1. [b] The assignment of $\nu_1$—$\nu_9$ has been taken from Ohwada (ref. 21). $\nu_l$ Denotes a lattice vibration; for the meaning of $\nu_x$ see text. [c] See Table 1. The infrared data have been taken from Ohwada (ref. 21).

## DISCUSSION

*General Discussion.*—In ref. 9 it has been argued that the luminescence of the investigated uranates originates from uranate centres near defects (traps). For this reason the vibrational structure which is observed in the emission spectra does not necessarily correspond to the vibrations of the intrinsic uranate groups. To determine to which trap a certain vibronic feature belonged, use was made of the temperature dependence of the luminescence (see also ref. 9). The assignments of the vibrational structure in the emission spectra of the uranates will be discussed in the following sections.

The decay curves of the emission of the uranates are not single-exponential, because they are a superposition of the decay curves of different traps. The decay times which are derived from the tails of the decay curves belong to traps which are not yet being emptied at 4.2 K. This means that these decay times can be regarded as radiative ones.

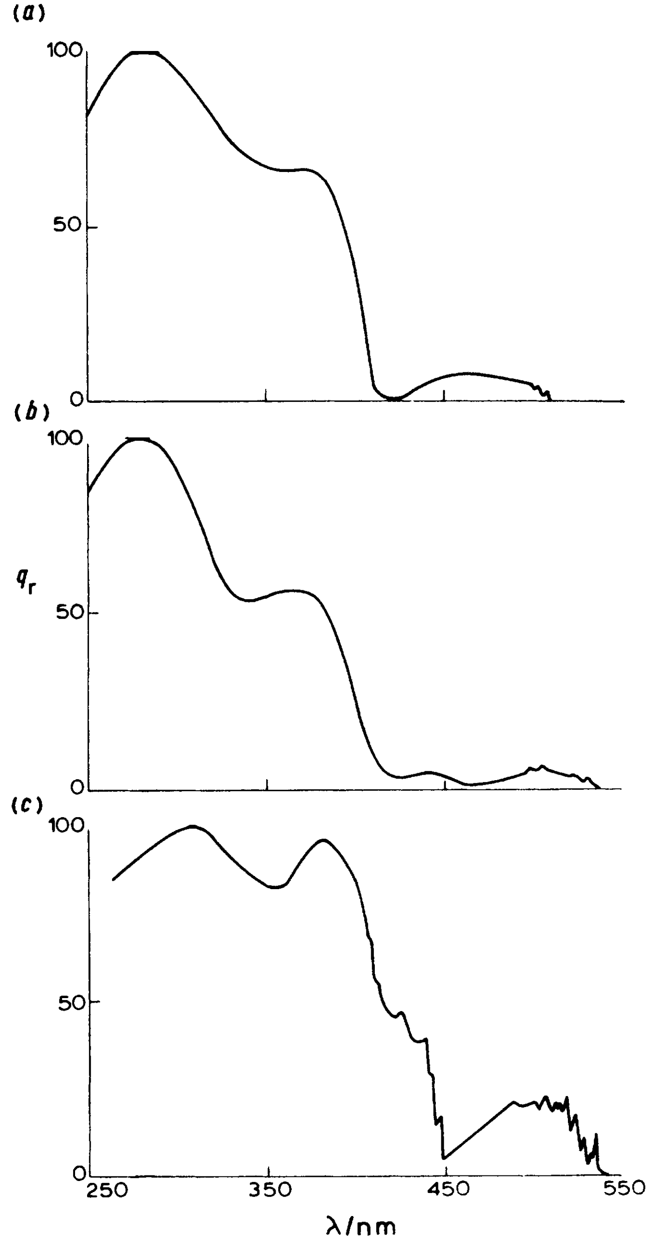

FIGURE 5 Excitation spectra of the green uranate luminescence of (*a*) $Ba_2CaUO_6$, (*b*) $Y_6UO_{12}$, and (*c*) $Li_4UO_5$, recorded at 4.2 K. In the case of $Y_6UO_{12}$ the excitation spectrum was obtained by monitoring the $Eu^{3+}$ luminescence of $(Y_{0.99}Eu_{0.01})_6UO_{12}$; $q_r$ denotes the relative quantum output in arbitrary units

TABLE 3

Assignment of the vibrational structure in the emission of $Li_2UO_4$

| λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ [a] | Assignment [b] | Vibr. freq./ cm$^{-1}$ [c] | Assignment [b] |
|---|---|---|---|---|
| 544.8 | 0 | a | R 32.5(w) | |
| 546.2 | 47 | b | R 173.3(w) | |
| 548.3 | 117 | c | i.r. 250(s) | U–$O_I$ bend |
| | | | R 267.5(w) | |
| 550.4 | b + 139 | b + $\nu_l$ | i.r. 285(m) | U–$O_I$ bend |
| 552.3 | c + 132 | c + $\nu_l$ | i.r. 305(m) | |
| 553.0 | b + 225 | b + U–$O_I$ bend | R 310(w) | |
| 555.0 | b + 290 | | i.r. 320(sh, m) | |
| 557.1 | c + 288 | c + U–$O_I$ bend | i.r. 340(m) | |
| 557.8 | b + 380 | | i.r. 380(sh, s) | |
| 558.1 | | | i.r. 405(m) | |
| 560.2 | c + 387 | | i.r. 425(m) | |
| 562.5 | b + 530 | b + U–$O_{II}$ str | i.r. 500(br, s) | U–$O_{II}$ str |
| 564.5 | c + 523 | c + U–$O_{II}$ str | R 700(s) | U–$O_I$ str |
| | | | i.r. 730(s) | |
| 567.8 | b + 969 | | i.r. 760(s) | |
| 568.9 | b + 730 | | | |
| 570.1 | b + 767,<br>c + 969 | b,c + U–$O_I$ str | | |
| 571.1 | c + 720 | | | |
| 572.4 | c + 760 | | | |
| 576.4 | c + 889 | | | |
| 577.2 | b + 983 | b,c + U–$O_I$ str + U–$O_I$ bend | | |
| 582.3 | c + 1 048 | | | |
| 596(br) | b,c + ≈1 500 | b,c + 2U–$O_I$ str | | |

[a] See Table 1. [b] Bend = bending mode, str = stretching mode. U–$O_I$ refers to the two primary U–O bonds and U–$O_{II}$ to the four equatorial U–O bonds. $\nu_l$ Denotes a lattice vibration.

The bands which are observed in the excitation spectra of the uranates are ascribed to charge-transfer transitions within the intrinsic uranate groups. The spectra of $Ba_2CaUO_6$, $Y_6UO_{12}$, and $Li_4UO_5$ are very similar to those observed for uranate groups in NaF, $Ba_2MgWO_6$, and $Sr_2MgWO_6$.[5] The assignments of the electronic transitions in the excitation spectra of $Ba_2CaUO_6$, $Y_6UO_{12}$, and $Li_4UO_5$ are presented in Table 5. These assignments are based on the assignments made for the $UO_6^{6-}$ group in NaF–U (uranium-activated sodium fluoride), which have also been included in Table 5. The deviation from $O_h$ symmetry is neglected here. The influence of symmetry lowering on the excitation spectra of $Y_6UO_{12}$ and $Li_4UO_5$ will be discussed in the following two sections.

It has already been mentioned that the excitation spectra of the luminescence of $Li_2UO_4$ and $MgUO_4$ are quite different from those observed for the other uranates. That no distinct bands are found for these compounds may be due to the fact that the $U^{6+}$ ions in $Li_2UO_4$ and $MgUO_4$ do not occupy a site with inversion symmetry. This results in a removal of the forbidden electric dipole (e.d.) character of part of the transitions and in a removal of the degeneracy of some of the excited states. This could give rise to many transitions with about equal intensity. The observed broad band could be due to a superposition of all these transitions.

The vibrational structure which has been observed in the excitation spectra of the investigated uranates has

TABLE 4

Assignment of the vibrational structure in the emission of $MgUO_4$

| λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ | Assignment [a] | Vibr. freq./cm$^{-1}$ [b] | Assignment [a] |
|---|---|---|---|---|
| 558.0 | 0 | a | i.r. 197(w) | U–$O_{II}$ bend |
| 560.3 | 73 | a + $\nu_l$ | i.r. 246(w) | U–$O_I$ bend |
| 563.4 | 172 | a + $\nu_l'$ | R 280(w) | |
| 564.7 | 212 | a + U–$O_I$ bend, U–$O_{II}$ bend | i.r. 285(w) | U–$O_I$ bend |
| 565.5 | 237 | | i.r. 350(w) | |
| 566.8 | 278 | | R 360(w) | |
| 567.4 | 297 | | R 410(w) | |
| 568.9 | 343 | | i.r. 415(br, m) | U–$O_{II}$ str |
| 569.6 | 365 | | i.r. 530(br, s) | |
| 570.5 | 392 | | R 530(m) | |
| 572.3 | 448 | a + U–$O_{II}$ str | i.r. 725(s) | U–$O_I$ str |
| 575.4 | 542 | | R 750(s) | |
| 581.3 | 718 | a + U–$O_I$ str | | |
| 582.6 | 757 | | | |
| 585.5(br) | 842 | a + U–$O_I$ str + $\nu_l$ | | |
| 590.9(br) | 998 | a + U–$O_I$ str + U–$O_I$ bend<br>a + U–$O_I$ str + U–$O_{II}$ bend | | |
| 593.9(br) | 1 083 | | | |
| 608.2(br) | 1 479 | a + 2U–$O_I$ str | | |

[a] See Table 3. The i.r. data have been taken from Ohwada (ref. 21). [b] See Table 1.

TABLE 5

Assignments of the electronic transitions observed in the excitation spectra of some uranates

| | NaF–U [b] | $Ba_2CaUO_6$ | | $Y_6UO_{12}$ | | $Li_4UO_5$ | |
|---|---|---|---|---|---|---|---|
| Assignment [a] | *E*/eV | λ/nm | *E*/eV | λ/nm | *E*/eV | λ/nm | *E*/eV |
| ${}^{12}\gamma_{8u}\rightarrow\gamma^{4}{}_{7u}$(m.d.) | 2.24 | 508.0 | 2.46 | 530.6<br>529.7 | 2.36 | 533.4<br>531.8 | 2.34 |
| ${}^{12}\gamma_{8u}\rightarrow{}^{13}\gamma_{8u}$(m.d.) | 2.72 | | | *ca.* 440 | *ca.* 2.9 | 446.0 | 2.80 |
| ${}^{12}\gamma_{8u}\rightarrow{}^{5}\gamma_{7u}$(m.d.) | 2.84 | | | | | | |
| ${}^{11}\gamma_{8g}\rightarrow{}^{4}\gamma_{7u}$(e.d.) | 3.10 | *ca.* 380 | *ca.* 3.3 | *ca.* 370 | *ca.* 3.4 | *ca.* 380 | *ca.* 3.3 |
| ${}^{11}\gamma_{8g},{}^{10}\gamma_{6g}\rightarrow$U(5*f*)(e.d.)<br>${}^{12}\gamma_{8u}\rightarrow$U(6*d*)(e.d.) | 3.5—5.5 | *ca.* 280 | *ca.* 4.5 | *ca.* 280 | *ca.* 4.5 | *ca.* 310 | *ca.* 4.0 |

[a] The orbitals denoted with ${}^{12}\gamma_{8u}$, ${}^{11}\gamma_{8g}$, and ${}^{10}\gamma_{6g}$ are orbitals with mainly O(2*p*) character. The orbitals denoted with ${}^{4}\gamma_{7u}$, ${}^{13}\gamma_{8u}$, and ${}^{5}\gamma_{7u}$ are orbitals with mainly U(5*f*) character. Transitions denoted with m.d. are magnetic-dipole allowed in $O_h'$; transitions denoted with e.d. are electric-dipole allowed in $O_h'$. [b] The assignments of the electronic transitions which have been observed in the excitation and absorption spectrum of NaF–U have been discussed in ref. 5. 1 eV ≈ 1.60 × $10^{-19}$ J.

not been analysed. For several reasons it was not possible to make unique assignments in these spectra. First of all the Xe lamp shows many lines in the spectral region where vibrational structure is observed. Furthermore an analysis of vibrational structure in the excitation spectra is difficult, because of the possibility of many different electronic transitions (see *e.g.* Table 5 and ref. 18).

In the following sections the luminescence spectra of $Y_6UO_{12}$, $Li_4UO_5$, $Li_2UO_4$, and $MgUO_4$ will be examined in some more detail.

$Y_6UO_{12}$.—An analysis of the emission spectrum of $Y_6UO_{12}$ is presented in Table 1. Each of the sharp lines in this spectrum (lines a, b, c, and d in Table 1) is ascribed to the electronic origin of the lowest transition within a certain trap. From Table 1 it appears that these electronic origins couple mainly with the ungerade vibrations ($\nu_6$, $\nu_4$, $\nu_3$) of the $UO_6^{6-}$ group. A progression is observed in the totally symmetric U–O stretching mode of 735 cm$^{-1}$. The assignments of the observed vibrational frequencies have been made by comparing the vibrational data of $Y_6UO_{12}$ with those of $Y_2O_3$ [19] and $Ba_2CaUO_6$.[20] The structure of $Y_2O_3$ is closely related to that of $Y_6UO_{12}$; $Ba_2CaUO_6$ contains isolated $UO_6^{6-}$ octahedra like $Y_6UO_{12}$. The notation of the vibrations with mainly U–O character is analogous to the notation of the vibrational modes of an octahedral complex. Because of the $S_6$ symmetry of the uranate groups in $Y_6UO_{12}$ the $T_{1u}$ ($\nu_3$ and $\nu_4$) and $T_{2g}$ ($\nu_5$) modes are split into two components: $T_{1u}\rightarrow A_u + E_u$ and $T_{2g}\rightarrow E_g + A_g$.

The vibrational structure in the emission of $Y_6UO_{12}$ can be described using the vibrations of the intrinsic uranate groups. This indicates that the traps are not very different from the intrinsic uranate groups.

In the previous section we have seen that the lowest electronic transition within $Y_6UO_{12}$ is assigned to a ${}^{12}\gamma_{8u}\rightarrow{}^{4}\gamma_{7u}$ transition. In $O_h$ symmetry this transition gives rise to three excited states with symmetry designations $E_g$, $T_{2g}$, and $T_{1g}$. Transitions from the $A_{1g}$ ground state to each of these excited states are electric-dipole (e.d.) forbidden. The $A_{1g}\rightarrow T_{1g}$ transition is magnetic-dipole (m.d.) allowed. Luminescence measurements on octahedral uranate groups in tungstates with the ordered perovskite structure show that the emission transition is a m.d. allowed transition.[4] This indicates

TABLE 6

Electronic transitions in the long-wavelength part of the excitation spectra of $Li_2UO_4$ and $MgUO_4$

| $Li_2UO_4$ | | $MgUO_4$ | |
|---|---|---|---|
| λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ | λ/nm | $\Delta\tilde{\nu}$/cm$^{-1}$ |
| 537.7 | 0 | 551.6 | 0 |
| 537.5 | 7 | 550.3 | 43 |
| 536.8 | 31 | | |
| 528.4 | 327 | 546.3 | 176 |

that the $T_{1g}$ state is the lowest excited state. In $Y_6UO_{12}$ the uranate groups have $S_6$ symmetry. The $T_{1g}$ excited state will, therefore, split into $E_g$ and $A_g$. The transitions from the $A_g$ ground state to both the $A_g$ and $E_g$ excited states are m.d. allowed.

From the excitation spectrum of $Y_6UO_{12}$ it appears that the electronic origin of the first excited state is split into two components with an energy difference of 32 cm$^{-1}$. It seems most probable that these two lines are due to transitions from the ground state ($A_g$) to the $A_g$ and $E_g$ components of the octahedral $T_{1g}$ state.

$Li_4UO_5$.—The emission spectrum of $Li_4UO_5$ looks rather complicated. First of all a large number of traps is observed (lines a—h in Table 2). Furthermore a progression is observed in a vibrational mode with a frequency of 770 cm$^{-1}$ ($\nu_x$). This vibration occurs neither in the i.r. nor in the Raman spectrum of $Li_4UO_5$. Ohwada[21] has made a normal-co-ordinate analysis of the vibrations of $Li_4UO_5$ by assuming a simple chain structure model, *viz.* $[UO_5]^{4-}{}_\infty$. The notation of the vibrational modes in Table 2 has been taken from Ohwada's work. A comparison of the vibronic features with the observed vibrational modes shows that these do not agree very well with each other. This suggests that the traps in $Li_4UO_5$ are rather different from the intrinsic uranate groups. The observed progression (770 cm$^{-1}$) could be due to the fact that the traps are uranate groups at the end of a chain, which would show a higher U–O$_{II}$ stretching frequency. The long value of the decay time ($\tau$ = 350 μs) indicates that for the traps the electronic transition in emission is not e.d. but m.d. allowed.

The excitation spectrum of the luminescence of $Li_4UO_5$ shows two structured bands. The electronic origin of the first band is split into two components with an energy difference of 56 cm$^{-1}$. In $Li_4UO_5$ the $U^{6+}$ ion occupies a site with $C_{4h}$ symmetry. In $C_{4h}$ the octahedral excited states, associated with the $^{12}\gamma_{8u} \rightarrow {}^4\gamma_{7u}$ transition, will split as follows: $E_g \rightarrow A_g + B_g$, $T_{2g} \rightarrow B_g + E_g$, and $T_{1g} \rightarrow A_g + E_g$. The transitions from the $A_g$ ground state to the $E_g$ and $A_g$ excited states are m.d. allowed. The two lines in the first excitation band are ascribed to m.d. allowed transitions from the ground state to the $A_g$ and $E_g$ components of the octahedral $T_{1g}$ state.

$Li_2UO_4$ *and* $MgUO_4$.—The emission and excitation spectra of $Li_2UO_4$ and $MgUO_4$ are very similar to each other. In both compounds the uranate groups can be regarded as uranyl groups (U–O$_I$) with four equatorial oxygen ions (U–O$_{II}$). The assignments in the emission spectra of $Li_2UO_4$ and $MgUO_4$ are presented in Tables 3 and 4, respectively. The lines denoted by a and a—c respectively are ascribed to electronic origins of transitions within different traps. In $MgUO_4$ only one trap is observed because the spectrum was recorded at 8 K. At this temperature the other traps which show luminescence at 4.2 K have already been emptied. The vibronic features can be reasonably well described with the vibrational modes of the intrinsic uranate groups. For both compounds it was not possible to determine in which U–O$_I$ stretching mode(s) the progression occurred. Ohwada[22,23] has assigned the features in the i.r. spectra of $Li_2UO_4$ and $MgUO_4$ to the vibrational modes of a $[UO_4]^{2-}{}_\infty$ layer and a $[UO_4]^{2-}{}_\infty$ chain, respectively. His assignments were based on a normal-co-ordinate analysis of the above mentioned structure models. We have measured both the i.r. and Raman spectra of one of these compounds, *viz.* of $Li_2UO_4$, and found more vibrational bands than allowed by the simple model of Ohwada. For this reason his assignments have not been taken over. Some of the vibrational frequencies of $Li_2UO_4$ and $MgUO_4$ have been assigned to U–O$_I$ and U–O$_{II}$ vibrations (see Tables 3 and 4).

The sharp features which are observed in the excitation spectra of both compounds (Table 6) are ascribed to electronic origins of transitions within the intrinsic uranate groups. These groups have $C_{2v}$ symmetry in $MgUO_4$ and $C_s$ symmetry in $Li_2UO_4$. The splitting of the $T_{1g}$ excited state is $T_{1g} \rightarrow A_2 + B_1 + B_2$ in the case of $MgUO_4$ and $T_{1g} \rightarrow A' + 2A''$ for $Li_2UO_4$. The transitions to the $B_1$ and $B_2$ states in $MgUO_4$ are e.d. as well as m.d. allowed, whereas the transition to the $A_2$ state is only m.d. allowed. In the case of $Li_2UO_4$ all transitions are both e.d. and m.d. allowed.

The lines at 551.6 and 550.3 nm, which are observed in the excitation spectrum of $MgUO_4$, are ascribed to transitions from the ground state to the $B_1$ and $B_2$ states of the octahedral $T_{1g}$ state. The line at 546.3 nm is tentatively ascribed to a transition from the ground state to one of the states with $T_{2g}$ or $E_g$ parentage.

In the case of $Li_2UO_4$ the lines at 537.7, 537.5, and 536.8 nm are ascribed to transitions from the ground state to the $A'$ and $A''$ states of the octahedral $T_{1g}$ state. The line at 528.4 is ascribed to a transition from the ground state to one of the components of the octahedral $T_{2g}$ or $E_g$ states.

The short radiative decay time of the luminescence of $MgUO_4$ and $Li_2UO_4$ ($\tau$ *ca.* 100 μs) as compared to that of the other uranates ($\tau$ *ca.* 300 μs) is in agreement with the e.d. character of the electronic transitions in $MgUO_4$ and $Li_2UO_4$.

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