Energy Transfer in Actinyl Compounds. Part 2.† Defect Centres in $Na[UO_2(OOCCH_3)_3]$

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Time-resolved fluorescence measurements and excitation spectroscopy of single crystals of $Na[UO_2(OOCCH_3)_3]$ at 4.2 K show the presence of two types of perturbed centre whose relative concentrations appear to be independent of the method of preparation. A model is proposed in which the sodium ions are partially disordered.

IN a recent comprehensive study of the electronic spectra of the uranyl ion [1] the low temperature single crystal absorption spectra, magnetic circular dichroism (m.c.d.), and natural circular dichroism (c.d.) of $Na[UO_2(OOCCH_3)_3]$ were used to identify the number of electronic excited states and, in some cases, their symmetries. These results and others [2] provided the basis for an interpretation of the electronic structure of the UO_2^{2+} ion.[3] A troublesome feature of the spectroscopy of sodium uranyl acetate is the observation, in the absorption spectrum, of a number of components within 30 cm^{-1} of the electronic origins which cannot be interpreted as phonon structure. We had assumed [1] that the consistent relative intensity of these satellite features, regardless of the method of crystal growth, indicated that they arose from factor group splittings. In emission five shallow traps have been observed [4] although it is not clear that any of these are of sufficient abundance to be responsible for the satellite absorption. In this paper we show, by means of time-resolved emission and excitation spectroscopy, that the satellite absorption is due to the same centre which leads to one of the trap emission bands. However there are also centres which can be described as anti-traps in the sense that their electronic energies lie above those of the bulk. We conclude that the omission of the satellite absorption from our previous analysis [1] is justified and that the number of electronic excited states derived from that analysis does not need to be modified.

EXPERIMENTAL

Large single crystals (4 × 4 × 4 mm) of $Na[UO_2(OOCCH_3)_3]$, usually taking the form of truncated octahedra, were grown either by slow cooling of saturated solutions in a Dewar flask from *ca.* 70 °C or by diffusion of a solution of uranyl nitrate into gels formed by the neutralisation of sodium metasilicate with acetic acid. The crystals were of a high degree of optical perfection.

The emission spectra were excited by a tunable, nitrogen-pumped dye laser (Molectron type DL200) operating at 20 Hz with a bandwidth of 0.5 cm^{-1} and a pulse length of *ca.* 5 ns. The emission was analysed by a Spex 1404 double monochromator. The time evolution of the luminescence was recorded by a Biomation 8 100 transient digitiser having a minimum digitisation interval of 10 ns and a 2 048 8-bit word memory. The results from successive laser pulses were averaged in real time by transfer of the data to a Research Machines Ltd. 380Z microcomputer *via* a fast parallel interface.[5] The excitation spectra of various emission features were obtained by integrating the total luminescence at the appropriate wavelength after each laser pulse and normalising the result with respect to the amplitude of the excitation pulse as recorded from a photodiode *via* the second channel of the digitiser.

The chemical purity of the samples was determined by infrared spectroscopy, chemical analysis, and thermogravimetric analysis. Crystals grown from D_2O solutions have identical i.r. spectra to those grown from H_2O, so that both water and CO(OH) groups cannot be present in the material. Similarly the thermogravimetric analysis excludes the presence of water in the crystal; the decomposition occurs by loss of acetate to generate $Na_2U_2O_7$.[6] Analysis of $Na[UO_2(OOCCH_3)_3]$: Found: C, 15.35; H, 1.75; Na, 4.80; U, 50.70. $C_6H_9NaO_8U$ requires C, 15.30; H, 1.90; Na, 4.90; U, 50.65%.

RESULTS

The time-resolved emission spectrum after excitation at 4 535.6 Å, Figure 1, consists of progressions in the UO_2 symmetric stretching frequency. It enables three types of emitting centre, with different time dependence, to be identified. For example the two features near 4 900 Å, which repeat near 5 120 Å, decay with a characteristic time scale of 10 μs whereas the relative intensity of the two features near 4 935 Å changes on a much longer time-scale.

The resolution of the emission bands allows the excitation spectrum of each of the three centres to be recorded independently (Figure 2). Each spectrum begins with a sharp feature, or features, which we take as either the electronic origin or two origins in close proximity. The centres are labelled (A), (B), and (C) in order of increasing energy of the first excited states.

The excitation spectrum of the (B) centre agrees well in most respects with the absorption spectrum of the bulk material (ref. 1, Figure 8). The energy of the first excited state is at 21 135 cm^{-1} corresponding to the label A_2 in the nomenclature of ref. 1. The origin of the (A) centre absorption occurs at 21 104.1 cm^{-1} and is identical with the satellite absorption labelled A_1 in ref. 1. Centre (C) has origins near 21 240 cm^{-1} and constitutes what we have termed an anti-trap.[7]

Because (A) and (C) are minority absorbers it cannot be assumed that their excitation spectra give a complete representation of their absorption spectra. The samples are not optically thin with respect to the absorption of the bulk (B) so that the mean flux incident on the minority centres is a function of the degree of absorption of (B) at the appropriate wavelength. Strong absorption by (B) will prevent the excitation of (A) and (C). Therefore, in comparing the

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† Part 1 is ref. 7.

spectra, only those features which are present, as opposed to those that are absent, are significant.

With this proviso it is evident that the main features of the spectra are very comparable. For example the spectrum of (A), although not completely separated from that of (B), clearly shows similar vibronic structure on its first electronic origin to that occurring on the equivalent transition in the bulk; the whole spectrum is shifted by 31.5 cm^{-1} to lower energy.

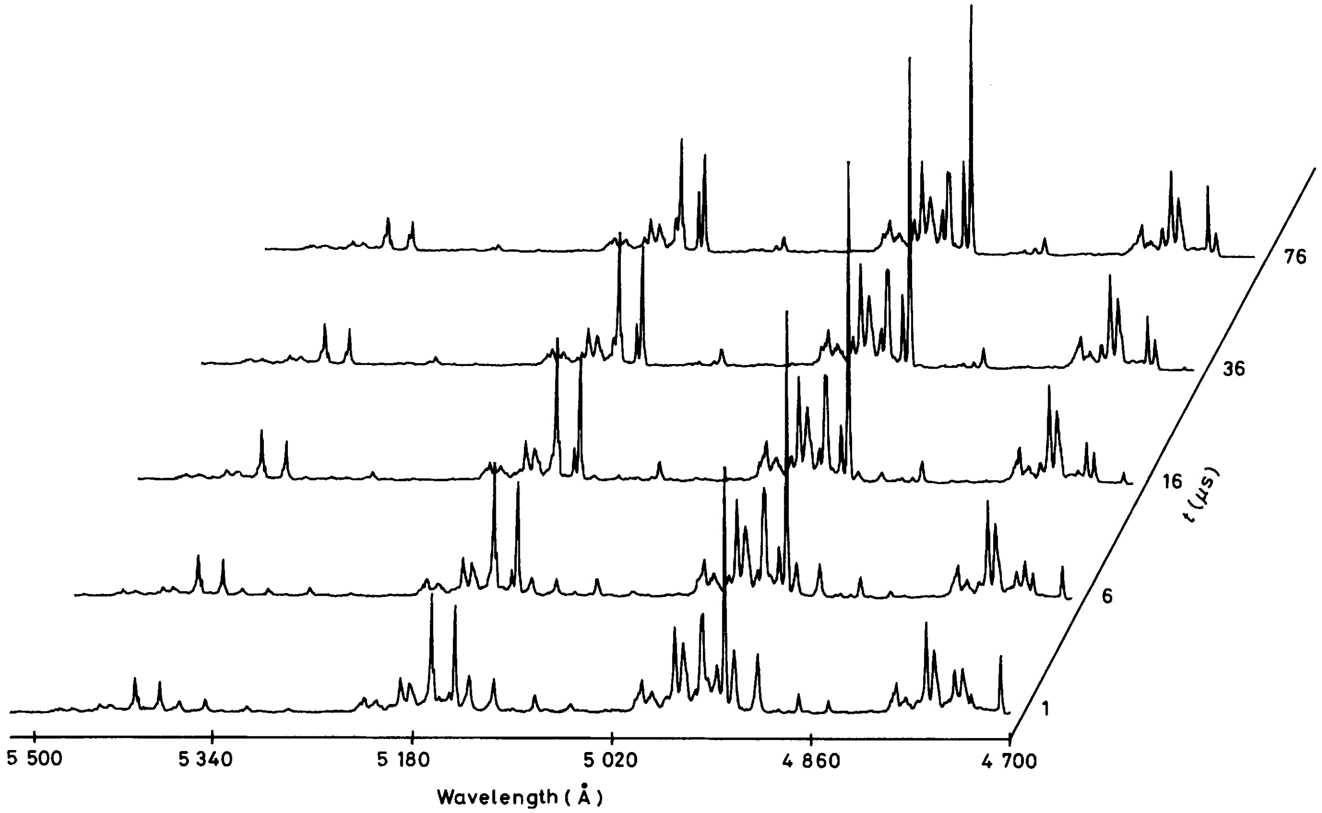

FIGURE 1 Time-resolved luminescence spectra of $Na[UO_2(OOCCH_3)_3]$ at 5 K

Near 4 560 Å the excitation spectrum of (A) is effectively cut off by the absorption of the bulk, but the progressions based on some of the features can be observed at wavelengths shorter than those illustrated in Figure 2.

The excitation spectrum of the (C) centres shows a strong resemblance to that of (A) despite an overall shift of 130 cm^{-1} to higher energy. Progressions based on many of the features in Figure 2 can be traced in the excitation spectra up to 4 250 Å. Table 1 summarises the observed energies of the electronic states associated with the three centres and the principal vibrational features built upon them. The nomenclature [1] in which the multiplicity of the components in the progressions has been analysed takes account of the interaction of the modes labelled $\nu_{sym.}$ and ν_n, which have the same symmetry. Features associated with the (C) centre are doubled and are reported in Table 1 as (C) and (C′). The linewidth of the emission is such that it is not possible to distinguish through the time dependence of their emission whether (C) and (C′) are distinct centres, or separate levels of a single centre. Both of the first two electronic excited states in $Na[UO_2(OOCCH_3)_3]$ are degenerate [1] so that it is possible that (C) and (C′) reflect the resolution of the degeneracy by the perturbation of the defect.

More information as to the nature of the three types of centre can be obtained from an analysis of the time-resolved emission spectra under high resolution. Figure 3 shows a portion of the emission spectrum, excited at the wavelength at which the (C) centres absorb, integrated over a period of 200 µs after the excitation pulse. Comparison with the spectra integrated over 50 µs and 2 ms, which emphasize the features of the (C) and (A) centres, respectively provides a straightforward assignment of the bands of the individual centres. The emission of (C) is split into two components. In Figure 3 the (B) emission is self-absorbed. The emission at wavelengths longer than those shown in Figure 3 resolves satellites to the (B) features, labelled (B) and (B′), which have slightly different progression fre-

TABLE 1

Site	Origin	Energy/cm^{-1}	Principal coupled modes *		
			ν_{sym}	ν_{asym}	ν_n
(A)	I	21 103.4	732	701.9	683.3
	II	21 903.3	—	—	680.3
					675.2
(B)	I	21 135.0	729	702.8	681.4
	II	21 915.3	—	—	—
(C)	I	21 325.6	—	—	—
	II	22 047.0	734.2	—	691.3
			725	—	678
(C′)	I	21 245.7	—	—	—
	II	22 061.6	739.6	—	691.3
			725	—	678.4

* For nomenclature see ref. 1.

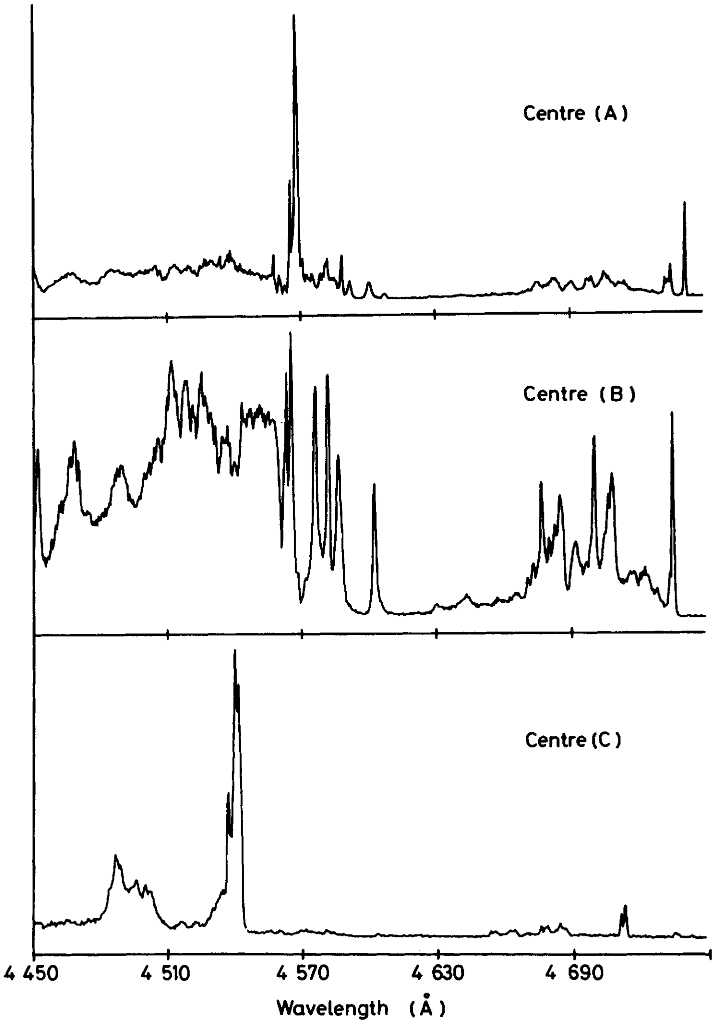

FIGURE 2 Luminescence excitation spectra of centres (A), (B), and (C) at 5 K

quencies to those of the bulk. They probably represent molecules removed by a lattice spacing from the defect sites. Table 2 summarises the observed sideband frequencies in emission and their progression frequencies.

DISCUSSION

The data in Table 2 illustrate that there are no major differences in the emission spectra of the three types of centre. Where they are observed the same vibronic features can be identified in each case. In particular the progression frequencies vary very little in association with the various sidebands, with the exception of the combination with the asymmetric UO_2 streching mode ν_{asym}, where appreciable anharmonic coupling is observed; the same is true in other cases.[2] Compared with the variation in ν_{sym} on any one centre there are appreciable differences in the frequencies on the (A) and (C) centres (848.7 and 847.6 cm^{-1}, respectively) as compared to the value for the bulk material (854.0 cm^{-1}). The perturbed sites apparently experience a small weakening of the UO bond.

Some conclusions may be drawn from the relative intensities in the emission spectra illustrated in Figure 4. The principal intensity lies in features associated with the symmetric and asymmetric UO_2 stretching frequencies, ν_{sym} and ν_{asym} respectively. The intensity of the bands involving only the symmetric stretching mode may be expected to reflect the small degree of electric dipole intensity statically introduced into an essentially parity forbidden transition, whereas those involving the asymmetric mode have an intensity related to the dynamic perturbation of this mode. It is unlikely that the dynamic mechanism is strongly perturbed in the defect centres so that the relative intensity observed for the two types of mode is a measure of the static intensity introduced into the pure electronic transition at the defect site. A comparison of these relative intensities for the (A) and (C) centres near 4 900 Å indicates an increase in the static intensity at the (A) centre. The comparison with the equivalent features of the bulk emission is difficult at this wavelength because of the presence of satellite structure due to the (B′) and (B″) centres.

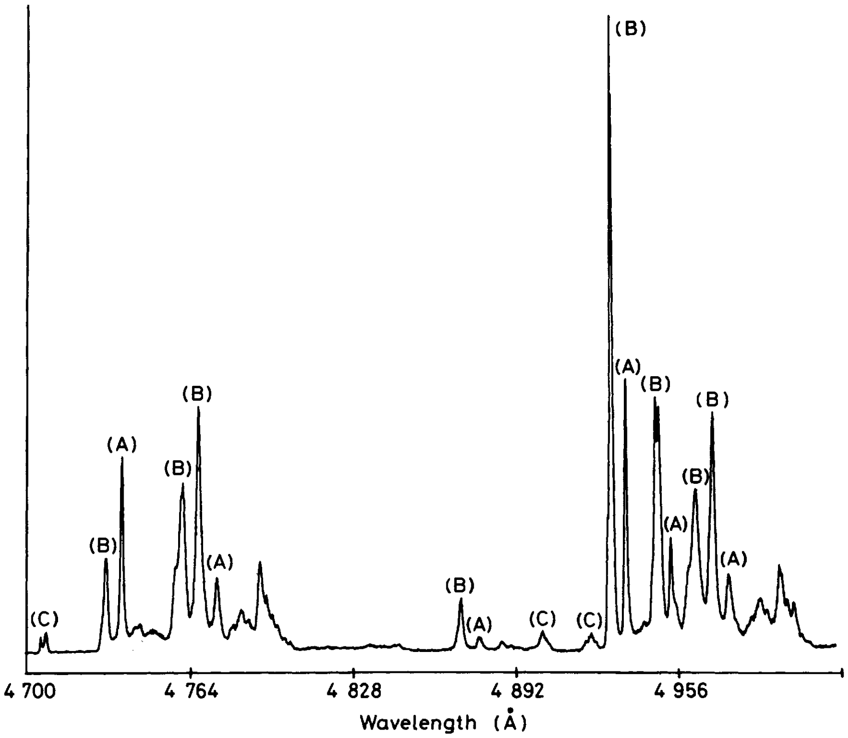

FIGURE 3 Luminescence spectrum at 5 K, integrated over 200 μs, excitation wavelength 4 535.6 Å

TABLE 2

Principal vibrational and progression intervals [a]

Site	Origin/cm^{-1}	ν_{sym}					ν_r	ν_b			ν_{asym}
(A)	21 102.3	0	—	133.9	—	164.7	240	267.2	606.2	—	921.2
	$-\nu_{sym}$	848.7	—	—	—	848.8	—	849.7	848.8	—	842.3
	$-2\nu_{sym}$	844.5	—	—	—	844.0	—	843.7	845.3	—	840.0
	$-3\nu_{sym}$	842.5	—	—	—	842.0	—	—	—	—	—
(B)	21 135.0	0	124.8	134.7	136.9	163.3	237.8	269.4	606.9	676.2	926.4
	$-\nu_{sym}$	853.6	854.6	—	853.6	854.6	854.7	853.1	856.3 [b]	854.5	850.1
	$-2\nu_{sym}$	852.3	850.4	—	852.3	851.9	852.3	854.3	850.9 [b]	853.1	846.9
	$-3\nu_{sym}$	848.5	—	—	849.7	849.1	849.3	848.2	—	—	—
(B′)	~21 135.0	0	—	—	—	—	—	—	—	—	922.3
	$-\nu$	849.5	—	—	—	—	—	—	—	—	847.7
	$-2\nu_{sym}$	850.8	—	—	—	—	—	—	—	—	844.8
	$-3\nu_{sym}$	847.4	—	—	—	—	—	—	—	—	—
(B″)	~21 135.0	0	—	—	—	—	—	—	—	—	931.5
	$-\nu_{sym}$	855.7	—	—	—	—	—	—	—	—	852.5
(C′)	21 235.6 [c]	0	—	—	—	163.4	—	—	—	—	927.4
(C″)	21 245.8 $-\nu_{sym}$	847.6	—	—	—	—	—	—	—	—	840.8
	$-2\nu_{sym}$	846.3	—	—	—	—	—	—	—	—	838.4

[a] For nomenclature see ref. 1. [b] Anomalous intervals due to Fermi resonance. [c] Intervals calculated from mean origin frequency.

Nevertheless it is clear from the spectra near 5 150 Å that, while both modes have similar intensities when they appear on the (B) centre, the static intensity is again relatively enhanced on the (A) centre. The static intensity on the (A) centre is approximately twice that in the bulk. We may then use the relative intensity of the (A) and (B) origins in absorption (1 : 10) to estimate that the relative abundance of the (A) centre is approximately 5%.

A careful assessment of the chemical and spectroscopic analyses of the material shows no evidence of chemical impurities with this abundance. It must therefore be assumed that the perturbed sites are to be associated with disorder in a chemically pure material.

The crystal structure of $Na[UO_2(OOCCH_3)_3]$ is known.[8] The material is cubic, space group $P2_13$, and is enantiomeric. There are four molecules per unit cell; each uranium atom lying at a C_3 site. The natural optical activity as observed in the c.d. spectrum [1] is attributable to the helical canting of the bidentate acetate chelate rings out of the equatorial plane. This distortion is responsible for the non-zero electric dipole transition moment in the first electronic origin, perpendicular to the C_3 axis. The natural c.d. of site (A) is so similar to that of the bulk sites [1] that the local stereochemistry of the chelate rings does not seem to be strongly affected. Because the vibrational data obtained from the emission spectrum also show no sign of the disruption of the immediate co-ordination sphere of the uranyl ion we assume that the complex anion $[UO_2(OOCCH_3)_3]^-$ retains its structural integrity in the defect sites. If this is true the only viable source of structural disorder lies in the displacement of the sodium ions.

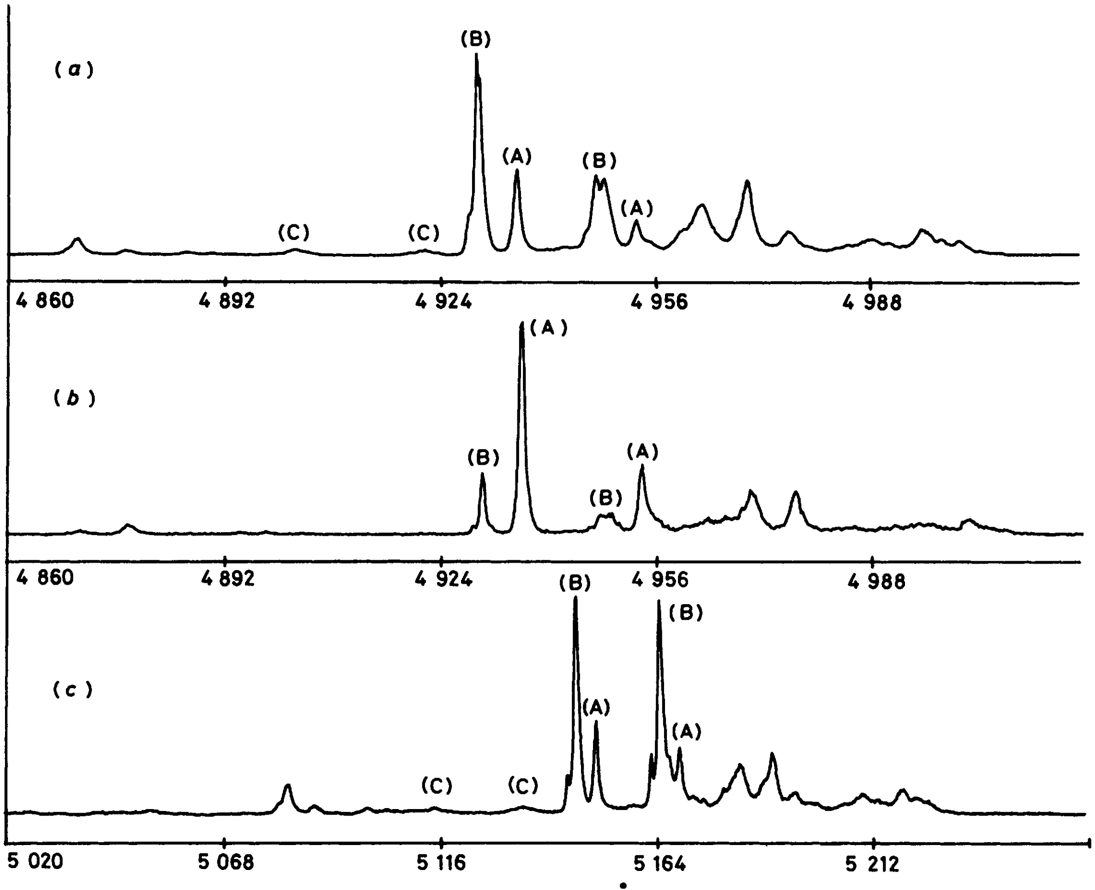

FIGURE 4 Luminescence spectrum at 5 K; (*a*) integrated over 200 μs, illustrating relative intensities in the (A) and (C) emission; (*b*) integrated over 2 ms, emphasizing relative intensities in the (A) emission; and (*c*) integrated over 200 μs illustrating the relative intensities of the (A) and (B) features

Normally the sodium ions occupy sites of almost octahedral symmetry, the ligands being carboxylate oxygen atoms. The sodium ions act as bridges between adjacent carboxylate chelate rings within the equatorial plane of the uranyl ions. Each sodium thereby links three complex anions. Within the unit cell four sodium ions are tetrahedrally disposed, lying on the three-fold axes. With respect to any one uranyl ion three of these sodium ions surround it slightly below the equatorial plane while the fourth lies well above the plane along the three-fold axis coincident with the O–U–O direction.

This situation can be discerned in Figure 5(*a*) which shows a view of the unit cell in the {110} direction. The atoms have been given their van der Waals radii. From this viewpoint a three-fold axis links the bottom right of the cell to the top left corner. On this axis a sodium ion occurs at the top left and a uranyl group just below the centre of the cell. A large empty volume occurs at the bottom right. Figure 5(*b*) shows the view along the {111} direction. At the centre of this view the central uranyl group is seen end on and the channel-like form of the empty region is clear. There are three additional vacancies related by symmetry to this volume. Figures 5(*c*) and 5(*d*) show these volumes occupied by spheres with a diameter of 4.00 Å, chosen so that they do not overlap with the surrounding atoms. There are no other voids of appreciable size within the structure.

The van der Waals diameter of sodium is 2.9 Å so that it is easily accommodated in the vacancies. We therefore propose that the disorder in the structure arises from the partial occupancy of these vacant pockets by sodium ions. Only a small change in the cation–cation repulsion occurs if the Na_I atom in Figure 5(*a*) is displaced along the {111} direction into the volume labelled V_{a_I} (V_a represents the vacancy occurring in the unit cell) [in Figure 5(*c*)] in the adjoining unit cell. In this location it lies close to the uranyl oxygen atom O_I in Figures 5(*a*) and 5(*b*) and also to the three carboxylate oxygen atoms of the original site, O_{II}. The vacancy has a cylindrical channel-like shape and is surrounded by a number of methyl hydrogen atoms and a further three carboxylate oxygen atoms, O_{III} [Figure 5(*b*)]. Assuming some deformation of the surrounding acetate groups this appears to be an electrostatically viable location for the sodium ion.

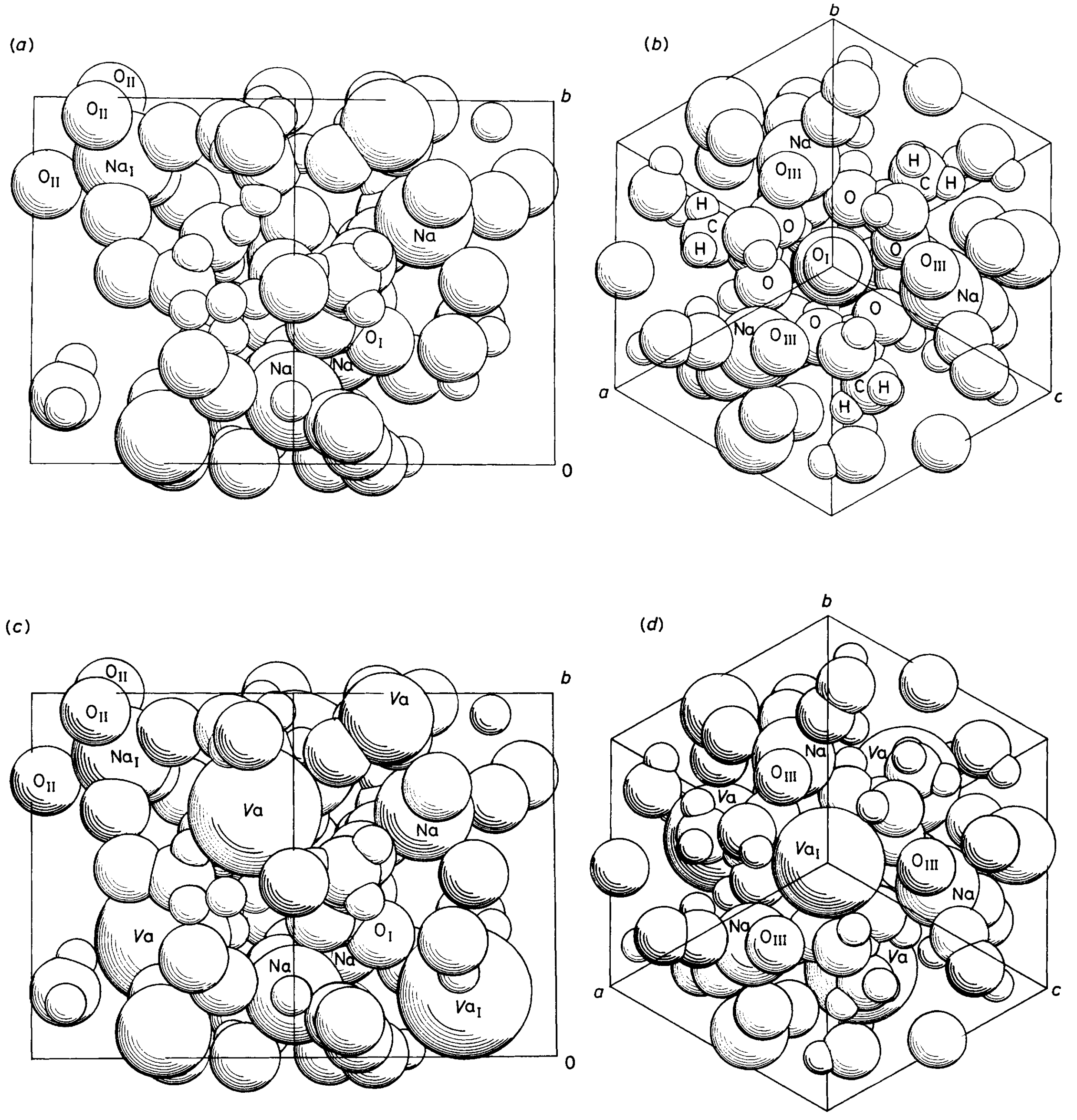

FIGURE 5 (*a*) Unit cell viewed in the {110} direction; (*b*) unit cell viewed in the {111} direction; (*c*) same as (*a*) showing vacancies of diameter 4.0 Å; (*d*) same as (*b*) showing vacancies of diameter 4.0 Å

This sodium displacement creates two types of defective uranyl centre simultaneously. There are three uranyl ions [type (*i*)] from whose equatorial plane the sodium ion has been withdrawn and a single uranyl ion [type(*ii*)] which is perturbed by a sodium ion lying close to and co-axial with the uranyl oxygen atom, O_I.

For type (*i*) ions it may be anticipated that the equatorial field of the ligands increases as a result of the removal of the competition of the sodium ion for the charge on the acetate oxygen atoms. This perturbation should raise the average energy of the metal *f* orbitals in the equatorial plane and raise the energy of the electronic transition (for the nature of the transition see ref. 3). We therefore associate the type (*i*) ion with the (C) spectroscopic centres. Consideration of the intensity mechanism for the first excited state [3] leads to the conclusion that a perturbation applied in the equatorial plane is less effective in providing electric dipole intensity than out-of-plane perturbations. It follows that no major change in static electric dipole intensity should be expected in the (C) centre.

Type (*ii*) ions can be expected to suffer an elongation of the uranyl-oxygen bond. Where cations compete for this oxygen atom lengthening of the bond is well established.[9] Furthermore the lengthening is accompanied by (*a*) a decrease in the U-O stretching frequency, and (*b*) a lowering in the energy of the first electronic excited state.[10] We therefore believe that the (A) centres should be identified as type (*ii*) ions. Because the perturbation lies perpendicular to the equatorial plane we may expect an appreciable increase in the static electric dipole intensity of the first excited state, as observed in the (A) centres. Finally it should be pointed out that type (*i*) and (*ii*) ions should always be present in the ratio 3 : 1 under this model. It follows that the (C) and (A) centres should always be present in this ratio. As far as we can judge from the intensity of their luminescence this is true of the samples which we have studied despite the fact that the crystals were grown by various techniques.

The discussion presented here supports the presence of an appreciable concentration, *ca.* 5%, of defects associated with displaced sodium ions. There is quite rapid energy transfer between the bulk and the traps. These observations account for the satellite features observed in absorption and imply that the number of electronic excited states previously assumed [1] is correct.

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