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Uranium–Oxygen Lattice Vibrations of Lithium and Sodium Uranates

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Received October 12, 1970

Normal-coordinate treatment of the optically active U–O lattice vibrations of lithium uranate, Li_4UO_5, and sodium uranate, Na_4UO_5, has been made on the assumption of a simple chain structure model of $(UO_5)_\infty{}^{4-}$. Based on the results of this treatment, some of the observed frequencies have been assigned to the U–O lattice vibrations. The force constants concerning U–O bonds and angles have been obtained and discussed in some detail. The effect of Li---O and Na---O interactions on the U–O lattice vibrations has also been discussed in terms of their force constants estimated from Badger's relationship.

Introduction

The infrared spectra of the metal uranates have been studied by several groups of workers in recent years.[1–5] However, the examination of the results has been limited in the normal-coordinate treatment based on a simple uranyl structure (O–U–O) assumed in various uranyl salts, and no quantitative interpretation of the results has therefore been attempted in detail. The purpose of the work reported here is to derive relations between the force constants and frequencies of the infrared-active and Raman-active U–O lattice vibrations of Li_4UO_5 and Na_4UO_5 and to give some interpretations of the observed frequencies of these crystals on the basis of their structures and the force constants.

The normal-coordinate treatment of the optically active lattice vibrations has been made by a method previously developed by Shimanouchi, Tsuboi, and Miyazawa.[6] The force constants concerning the U–O bonds and angles have been obtained and discussed.

Normal-Coordinate Treatment

The crystal structures of Li_4UO_5 and Na_4UO_5 have been determined by X-ray and neutron diffraction measurements.[1,7] According to them, both these crystals are body centered tetragonal and belong to space group $I4/m\text{-}C_{4h}{}^5$. Each uranium is bonded to six oxygens, two of which (parallel to the z axis) are more weakly bonded than the remaining four oxygens lying in the xy plane. The crystal lattice consists of parallel chains of infinite $(UO_5)_\infty{}^{4-}$ octahedra joined by sharing corners. The structure of the infinite $(UO_5)_\infty{}^{4-}$ chains is shown in Figures 1 and 2(a). The alkali atoms are situated between the chains and bind the chains together as shown in Figure 2(b).

As a preliminary study of the normal-coordinate treatment of the U–O lattice vibrations for Li_4UO_5 and Na_4UO_5, we first consider the smallest unit cell containing one uranium atom and five oxygen atoms on the assumption of the infinite-chain structure of $(UO_5)_\infty{}^{4-}$ (point group D_{4h}) neglecting alkali atoms. The effect of Li---O and Na---O interactions on the U–O lattice modes will be discussed in terms of their force constants estimated from Badger's relationship.[8] It is shown by the group theoretical treatment that, for the infinite $(UO_5)_\infty{}^{4-}$ chain, there should be ten fundamental lattice vibrations, *i.e.*, one A_{1g} (Raman active), two A_{2u} (infrared active), one B_{1g} (Raman active), one B_{2g} (Raman active), one B_{2u} (inactive), one E_g (Raman active), and three E_u (infrared active) vibrations.

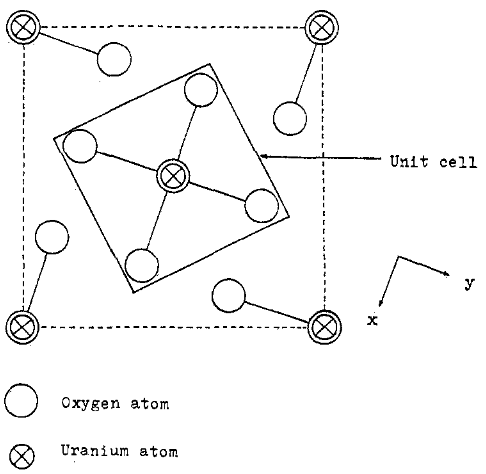

Figure 1.—Structure of the infinite $(UO_5)_\infty{}^{4-}$ chain viewed along the z axis.

The optically active Cartesian coordinates X_{op} and the optically active internal coordinates R_{op} are taken as follows: X_{op}: Δx_U, Δy_U, Δz_U, Δx_1, Δy_1, Δz_1, Δx_2, Δy_2, Δz_2, Δx_3, Δy_3, Δz_3, Δx_4, Δy_4, Δz_4, Δx_5, Δy_5, Δz_5. R_{op}: Δr_1, Δr_2, Δr_3, Δr_4, Δr_5, $\Delta r_5'$, $\Delta\phi_{12}$, $\Delta\phi_{23}$, $\Delta\phi_{34}$, $\Delta\phi_{41}$, $\Delta\phi_{51}$, $\Delta\phi_{52}$, $\Delta\phi_{53}$, $\Delta\phi_{54}$, $\Delta\phi_{5'1}$, $\Delta\phi_{5'2}$, $\Delta\phi_{5'3}$, $\Delta\phi_{5'4}$, $\Delta\phi_{5x}$, $\Delta\phi_{5y}$. Here, r's and ϕ's are the U–O bond distances and the bond angles around the uranium and oxygen atoms as shown in Figure 2(a). The inverse kinetic energy matrix $G^c{}_{op}$ for the optically active vibrations is given with respect to the optically active Cartesian coordinates as

$$\begin{aligned} G^c{}_{op}(i,i) &= \mu_U, \quad i = 1\text{–}3 \\ G^c{}_{op}(k,k) &= \mu_O, \quad k = 4\text{–}18 \\ G^c{}_{op}(i,j) &= 0, \quad i \neq j \ (i,j = 1\text{–}18) \end{aligned} \tag{1}$$

where μ_U and μ_O are the reciprocal masses of uranium and oxygen atoms, respectively.

On the other hand, for obtaining the corresponding potential energy matrix $F^c{}_{op}$, we need a transformation matrix B_{op} which is defined by

$$R_{op} = B_{op}X_{op} \tag{2}$$

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(1) H. R. Hoekstra and S. Siegel, *J. Inorg. Nucl. Chem.*, **26**, 693 (1964).

(2) J. G. Allpress, *ibid.*, **26**, 1847 (1964).

(3) H. R. Hoekstra, *ibid.*, **27**, 801 (1965).

(4) D. Jakes, *et al.*, *ibid.*, **30**, 525 (1968).

(5) L. H. Jones, *Spectrochim. Acta*, **11**, 409 (1959).

(6) T. Shimanouchi, M. Tsuboi, and T. Miyazawa, *J. Chem. Phys.*, **35**, 1597 (1961).

(7) L. M. Kovba, *Zh. Strukt. Khim.*, **3**, 159 (1962).

(8) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

$$B_{op} = \left[\begin{array}{c|cccccccccccccccccc} & \Delta x_U & \Delta y_U & \Delta z_U & \Delta x_1 & \Delta y_1 & \Delta z_1 & \Delta x_2 & \Delta y_2 & \Delta z_2 & \Delta x_3 & \Delta y_3 & \Delta z_3 & \Delta x_4 & \Delta y_4 & \Delta z_4 & \Delta x_5 & \Delta y_5 & \Delta z_5 \\ \Delta r_1 & 1 & & & -1 & & & & & & & & & & & & & & \\ \Delta r_2 & & 1 & & & & & & -1 & & & & & & & & & & \\ \Delta r_3 & -1 & & & & & & & & & 1 & & & & & & & & \\ \Delta r_4 & & -1 & & & & & & & & & & & & 1 & & & & \\ \Delta r_5 & & & 1 & & & & & & & & & & & & & & & -1 \\ \Delta r_{5'} & & & -1 & & & & & & & & & & & & & & & 1 \\ \Delta\phi_{12} & -\rho_1 & -\rho_1 & & & \rho_1 & & \rho_1 & & & & & & & & & & & \\ \Delta\phi_{23} & \rho_1 & -\rho_1 & & & & & -\rho_1 & & & & \rho_1 & & & & & & & \\ \Delta\phi_{34} & \rho_1 & \rho_1 & & & & & & & & & -\rho_1 & & -\rho_1 & & & & & \\ \Delta\phi_{41} & -\rho_1 & \rho_1 & & & -\rho_1 & & & & & & & & \rho_1 & & & & & \\ \Delta\phi_{51} & -\rho_2 & & -\rho_1 & & & & & \rho_1 & & & & & & & & \rho_2 & & \\ \Delta\phi_{52} & & -\rho_2 & -\rho_1 & & & \rho_1 & & & & & & & & & & & \rho_2 & \\ \Delta\phi_{53} & \rho_2 & & -\rho_1 & & & & & & & & & \rho_1 & & & & -\rho_2 & & \\ \Delta\phi_{54} & & \rho_2 & -\rho_1 & & & & & & & & & & & & \rho_1 & & -\rho_2 & \\ \Delta\phi_{5'1} & -\rho_2 & & \rho_1 & & & -\rho_1 & & & & & & & & & & \rho_2 & & \\ \Delta\phi_{5'2} & & -\rho_2 & \rho_1 & & & & & & -\rho_1 & & & & & & & & \rho_2 & \\ \Delta\phi_{5'3} & \rho_2 & & \rho_1 & & & & & & & & & -\rho_1 & & & & -\rho_2 & & \\ \Delta\phi_{5'4} & & \rho_2 & \rho_1 & & & & & & & & & & & & -\rho_1 & & -\rho_2 & \\ \Delta\phi_{5x} & -2\rho_2 & & & & & & & & & & & & & & & 2\rho_2 & & \\ \Delta\phi_{5y} & & -2\rho_2 & & & & & & & & & & & & & & & 2\rho_2 & \end{array}\right] \quad (3)$$

The B_{op} matrix is then calculated as shown in eq 3. In this matrix, ρ_1 $(=1/r_1)$ and ρ_2 $(=1/r_2)$ are the reciprocal equilibrium distances of primary and secondary U–O bonds, respectively. Using this B_{op} matrix, the $F^c{}_{op}$ matrix is given by the relation

$$F^c{}_{op} = (B_{op})^t F^i{}_{op} B_{op} \quad (4)$$

Here, $F^i{}_{op}$ is the potential energy matrix expressed in terms of the optically active internal coordinates R_{op}, and superscript t means transposed matrix. The potential energy V of the $(UO_5)_\infty{}^{4-}$ chain lattice under the assumption of a simple valence force field may be given by

$$\begin{aligned} 2V = {} & K_1[(\Delta r_1)^2 + (\Delta r_2)^2 + (\Delta r_3)^2 + (\Delta r_4)^2] + \\ & K_2[(\Delta r_5)^2 + (r_{5'})^2] + H_1[(\Delta\phi_{12})^2 + (\Delta\phi_{23})^2 + \\ & (\Delta\phi_{34})^2 + (\Delta\phi_{41})^2] + H_2[(\Delta\phi_{51})^2 + (\Delta\phi_{52})^2 + \\ & (\Delta\phi_{53})^2 + (\Delta\phi_{54})^2 + (\Delta\phi_{5'1})^2 + (\Delta\phi_{5'2})^2 + \\ & (\Delta\phi_{5'3})^2 + (\Delta\phi_{5'4})^2] + H_3[(\Delta\phi_{5x})^2 + (\Delta\phi_{5y})^2] \end{aligned} \quad (5)$$

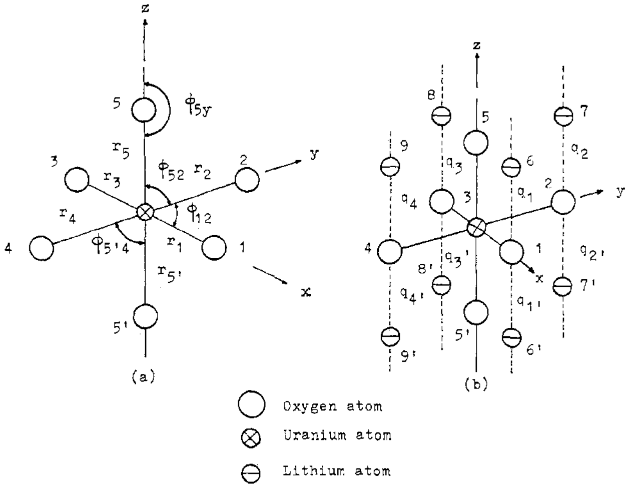

Figure 2.—(a) Structure of the infinite $(UO_5)_\infty{}^{4-}$ chain assumed in Li_4UO_5 and Na_4UO_5. (b) Structure of the infinite Li_4UO_5 chain.

where K_1 and K_2 denote the stretching force constants of primary and secondary U–O bonds, and H_1, H_2, and H_3 denote the bending force constants around the uranium and oxygen atoms. The $F^i{}_{op}$ matrix is therefore given as a 20th-order diagonal matrix with the elements of K_1, K_2, H_1, H_2, and H_3.

Based on the symmetry of the $(UO_5)_\infty{}^{4-}$ chain structure (point group D_{4h}), the $G^c{}_{op}$ and $F^c{}_{op}$ may be factored by a proper choice of optically active Cartesian symmetry coordinates S_{op}, which are given by

$$S_{op} = UX_{op} \quad (6)$$

Here, the S_{op} coordinates are chosen as shown in eq 7.

$$S_1 = \frac{1}{2}(\Delta x_1 + \Delta y_2 - \Delta x_3 - \Delta y_4)$$

$$S_2 = \frac{1}{\sqrt{30}}(5\Delta z_U - \Delta z_1 - \Delta z_2 - \Delta z_3 - \Delta z_4 - \Delta z_5)$$

$$S_3 = \frac{1}{\sqrt{20}}(-\Delta z_1 - \Delta z_2 - \Delta z_3 - \Delta z_4 + 4\Delta z_5)$$

$$S_4 = \frac{1}{2}(\Delta x_1 - \Delta y_2 - \Delta x_3 + \Delta y_4)$$

$$S_5 = \frac{1}{2}(\Delta y_1 + \Delta x_2 - \Delta y_3 - \Delta x_4)$$

$$S_6 = \frac{1}{2}(\Delta z_1 - \Delta z_2 + \Delta z_3 - \Delta z_4)$$

$$S_7 = \frac{1}{2}(\Delta z_1 + \Delta z_2 - \Delta z_3 - \Delta z_4)$$

$$S_8 = \frac{1}{2}(\Delta z_1 - \Delta z_2 - \Delta z_3 + \Delta z_4)$$

$$S_9 = \frac{1}{\sqrt{30}}(5\Delta x_U - \Delta x_1 - \Delta x_2 - \Delta x_3 - \Delta x_4 - \Delta x_5)$$

$$S_{10} = \frac{1}{\sqrt{20}}(-\Delta x_1 - \Delta x_2 - \Delta x_3 - \Delta x_4 + 4\Delta x_5)$$

$$S_{11} = \frac{1}{2}(\Delta x_1 - \Delta x_2 + \Delta x_3 - \Delta x_4)$$

$$S_{12} = \frac{1}{\sqrt{30}}(5\Delta y_U - \Delta y_1 - \Delta y_2 - \Delta y_3 - \Delta y_4 - \Delta y_5)$$

$$S_{13} = \frac{1}{\sqrt{20}}(-\Delta y_1 - \Delta y_2 - \Delta y_3 - \Delta y_4 + 4\Delta y_5)$$

$$S_{14} = \frac{1}{2}(\Delta y_1 - \Delta y_2 + \Delta y_3 - \Delta y_4)$$

$$S_{15} = \frac{1}{\sqrt{6}}(\Delta x_U + \Delta x_1 + \Delta x_2 + \Delta x_3 + \Delta x_4 + \Delta x_5)$$

$$S_{16} = \frac{1}{\sqrt{6}}(\Delta y_U + \Delta y_1 + \Delta y_2 + \Delta y_3 + \Delta y_4 + \Delta y_5)$$

$$S_{17} = \frac{1}{\sqrt{6}}(\Delta z_U + \Delta z_1 + \Delta z_2 + \Delta z_3 + \Delta z_4 + \Delta z_5)$$

$$S_{18} = \frac{1}{2}(-\Delta y_1 + \Delta x_2 + \Delta y_3 - \Delta x_4) \qquad (7)$$

In these, the symmetry coordinate S_1 is the A_{1g} type vibration. Those of S_2 and S_3 are two A_{2u} type vibrations, S_4 is the B_{1g} type vibration, S_5 is the B_{2g} type vibration, S_6 is the B_{2u} type vibration, S_7 and S_8 are one E_g type vibration, and S_9, S_{10}, S_{11}, S_{12}, S_{13}, and S_{14} are three E_u type vibrations. The S_{15}, S_{16}, and S_{17} coordinates are the redundant coordinates. The S_{18} coordinate is also redundant on the assumption of the $(UO_5)_\infty{}^{4-}$ chain structure since S_{18} represents a rotation of the infinite one-dimensional chain about its axis. Based on these symmetry coordinates, the approximate vibration modes may be drawn as in Figure 3. The inverse kinetic energy matrix $G^{cs}{}_{op}$ and the potential energy matrix $F^{cs}{}_{op}$ expressed in terms of the S_{op} coordinates are obtained by the relations

$$G^{cs}{}_{op} = UG^{c}{}_{op}U^t \qquad (8)$$

and

$$F^{cs}{}_{op} = UF^{c}{}_{op}U^t \qquad (9)$$

From these two equations, the $G^{cs}{}_{op}$ and $F^{cs}{}_{op}$ are obtained as shown in eq 10 and 11, where $A = F = K_1$, $B = (12/5)(K_2 + (4H_2/r_1^2))$, $C = (2/5)(K_2 + (H_2/r_1^2))$, $D = (4\sqrt{6}/5)(-K_2 + (H_2/r_1^2))$, $E = (4H_1/r_1^2)$, $G = H = (2H_2/r_1^2)$, $I = (12/5)(K_1 + (2H_1/r_1^2) + (2H_2/r_2^2) + (2H_3/r_2^2))$, $J = (1/10)(K_1 + (2H_1/r_1^2) + (32H_2/r_2^2) + (32H_3/r_2^2))$, $K = (1/2)(K_1 + (2H_1/r_1^2))$, $L = (\sqrt{6}/5)(K_1 + (2H_1/r_1^2) - (8H_2/r_2^2) - (8H_3/r_2^2))$, $M = (\sqrt{5}/10)(-K_1 + (2H_1/r_1^2))$, $N = (\sqrt{30}/5)(-K_1 + (2H_1/r_1^2))$.

$$\begin{aligned} G^{cs}{}_{op}(i,i) &= 0, \quad i = 15, 16, 17, 18 \\ G^{cs}{}_{op}(k,k) &= \frac{5\mu_U + \mu_O}{6}, \quad k = 2, 9, 12 \\ G^{cs}{}_{op}(l,l) &= \mu_O, \quad l = 1, 3\text{–}8, 10, 11, 13, 14 \\ G^{cs}{}_{op}(i,j) &= 0, \quad i \neq j \ (i,j = 1\text{–}18) \end{aligned} \qquad (10)$$

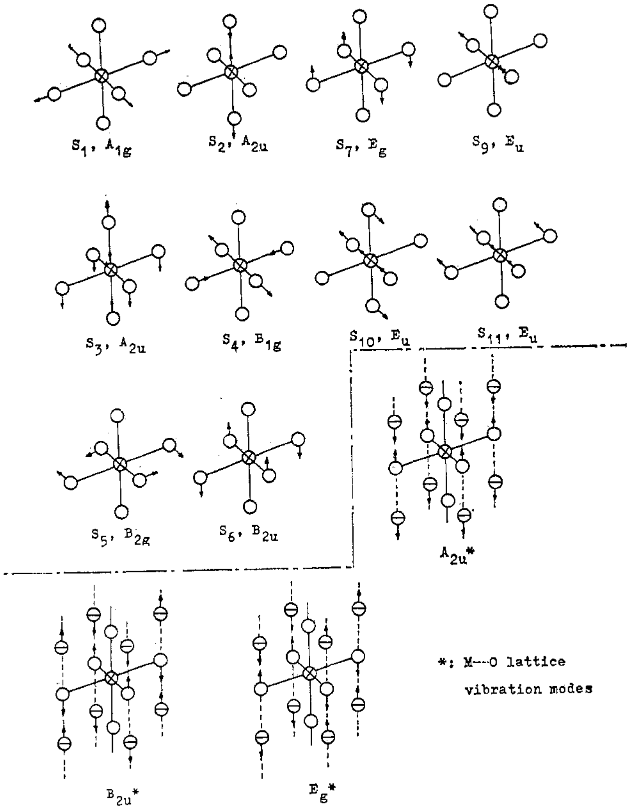

Figure 3.—Approximate vibration modes along the symmetry coordinates.

The secular equation for calculation of the optically active normal frequencies is finally obtained as

$$|G^{cs}{}_{op}F^{cs}{}_{op} - E\lambda| = 0$$

where E is the unit matrix with the same order as that of the $G^{cs}{}_{op}$ and $F^{cs}{}_{op}$ matrices.

Discussions on the Observed Frequencies and Force Constants

The infrared spectra of crystalline Li_4UO_5 and Na_4UO_5 have been measured in the region of 4000–250 cm^{-1} by Hoekstra.[1] However, the far-infrared and Raman spectra of such crystals have unfortunately not been obtained. The observed frequencies for Li_4UO_5 and Na_4UO_5 are listed in Table I. The broad strong band at 590 cm^{-1} is certainly assigned to the E_u type vibration (ν_8) which is tentatively ascribed to the asymmetric stretching vibration in the $(UO_4)_\infty{}^{2-}$ plane as

$$F^{cs}{}_{op} = \begin{array}{cccccccccccccc} S_1 & S_2 & S_3 & S_4 & S_5 & S_6 & S_7 & S_8 & S_9 & S_{10} & S_{11} & S_{12} & S_{13} & S_{14} \end{array}$$
$$\left[\begin{array}{cccccccccccccc} A & & & & & & & & & & & & & \\ & B & D & & & & & & & & & & & \\ & & C & & & & & & & & & & & \\ & & & E & & & & & & & & & & \\ & & & & F & & & & & & & & & \\ & & & & & G & & & & & & & & \\ & & & & & & H & & & & & & & \\ & & & & & & & H & & & & & & \\ & \text{symmetric} & & & & & & & I & L & N & & & \\ & & & & & & & & & J & M & & & \\ & & & & & & & & & & K & & & \\ & & & & & & & & & & & I & L & N \\ & & & & & & & & & & & & J & M \\ & & & & & & & & & & & & & K \end{array}\right] \qquad (11)$$

TABLE I

OBSERVED AND CALCULATED FREQUENCIES (CM^{-1}) OF Li_4UO_5 AND Na_4UO_5

	Li_4UO_5			Na_4UO_5		
Species	Obsd	Calcd-1[a]	Calcd-2[b]	Obsd	Calcd-1[a]	Calcd-2[b]
A_{1g}, ν_1		555	555		555	555
A_{2u}, ν_2	430	430	430	410	410	410
ν_3	292	292	292	260	260	200
			624			465
B_{1g}, ν_4		555	555		555	555
B_{2g}, ν_5[c]		366	443		326	421
B_{2u}, ν_6		259	249		231	160
			622			455
E_g, ν_7		259	249		231	160
			622			455
E_u, ν_8	590	590	590	590	590	590
ν_9	333	333	333	350	350	350
ν_{10}[c]		276	333		246	317

[a] These frequencies were calculated on the basis of the infinite $(UO_5)_\infty{}^{4-}$ chain model. [b] These frequencies were calculated on the basis of the simple chain structure model including the main Li---O and Na---O interactions. For each compound, three vibrational frequencies are added anew. The other frequencies which are group theoretically expected become zero from the assumption of the simple chain structure model and neglect of the weak interactions of Li---O and Na---O. [c] These frequencies are somewhat arbitrary since $H_1 \approx H_2$ was assumed.

TABLE II

FORCE CONSTANTS (MDYN/Å) OF Li_4UO_5 AND Na_4UO_5

	Li_4UO_5		Na_4UO_5	
	Set 1[a]	Set 2[b]	Set 1[a]	Se 2[b]
K_1	2.900	2.900	2.900	2.900
K_2	0.816	0.816	0.741	0.741
$H_1\rho_1{}^2$	0.316	0.462	0.251	0.417
$H_1\rho_1{}^2$	0.316	0.462	0.251	0.417
$(H_2 + H_3)\rho_2{}^2$	0.613	0.613	0.676	0.676
f	0	0.500	0	0.400

[a] Force constants of infinite $(UO_5)_\infty{}^{4-}$ chain assumed in Li_4UO_5 and Na_4UO_5. [b] Force constants including the Li---O and Na---O interactions.

shown in Figure 3, S_9. The band in the region of 430–410 cm^{-1} may be assigned to the A_{2u} type vibration (ν_2) due to the asymmetric stretching vibration in the endless chain –O–U–O–U– as given in Figure 3, S_2. These two assignments seem most reasonable from a consideration of the bond distances of primary U–O (1.99 Å) in the $(UO_4)_\infty{}^{2-}$ plane and secondary U–O (2.32–2.23 Å) in the endless –O–U–O–U– chain.

The lower frequency between 333 and 350 cm^{-1}, which has already been stated to be the out-of-plane bending vibration (A_{2u}, ν_3) of the primary U–O bond by Hoekstra, should be assigned to the E_u type bending vibration (ν_9) of the endless chain –O–U–O–U– as shown in Figure 3, S_{10}. This may be supported by taking into account the case of α-UO_3 having a similar type of the endless chain –O–U–O–U–.[9] Also, the lowest frequency in the region of 292–260 cm^{-1}, which has previously been assigned to the bending vibration of the endless chain, should be assigned to the out-of-plane bending vibration of the A_{2u} type (ν_3) given in Figure 3, S_3. This type vibration corresponds to the primary U–O bending vibration occurring in the region of 290–250 cm^{-1} for the metal monouranates such as MUO_4 and M_2UO_4 (M = mono- and divalent metals).[10] In addition, it is expected that the infrared-active band ν_{10}, corresponding to the E_u type vibration, which has not been reported in the literature, may be observed in the far-infrared region below 300 cm^{-1}. The above assignments may finally be supported by the calculation of normal vibration frequencies.

We adjusted the force constants so that the calculated frequencies give the best agreement with the observed ones. The force constants adjusted are given in Table II (set 1). Also, it was assumed in the frequency calculation that the $(\mu_U)^2$ and $(\mu)_U{}^3$ are approximately equal to zero since the effect of the $(\mu_U)^2$ and $(\mu_U)^3$ on the calculated results is negligibly small. The results of the calculation on the basis of the force constants in Table II (set 1) and the above approximation are shown in Table I and compared with the observed frequencies obtained by Hoekstra.[1] The agreement between the observed and calculated frequencies in Table I is exact. However, as the bending force constant H_1 around the uranium atom cannot be determined directly for lack of the E_u type vibration frequency (ν_{10}), we unavoidably assumed that $H_1 \approx H_2$. For that reason, the frequencies of ν_5 and ν_{10} calculated mainly from the force constant H_1 are somewhat arbitrary.

The foregoing interpretations based on the infinite $(UO_5)_\infty{}^{4-}$ chain model can well explain only the locations of the infrared-active bands of the Li_4UO_5 and Na_4UO_5 crystals. However, the variations in the band widths near 590 cm^{-1} for Li_4UO_5 and near 410 cm^{-1} for Na_4UO_5[1] cannot be explained, in detail, from the above argument. In order to obtain further information on this, more rigorous treatment including the Li---O and Na---O interaction terms will be necessary as discussed below.

On this treatment, the chain structure model including four Li atoms or four Na atoms in the smallest unit cell as shown in Figure 2(b) is employed. Though the O---Li---O bonds along the z axis in this structure are collinear, the O---Na---O bonds are somewhat bent. However, it is assumed in the present normal-coordinate treatment that the O---Na---O bonds are collinear as in the case of the O---Li---O bonds. Group theory shows the following modes for the model: $2\ A_{1g} + 2\ A_{2g} + 3\ A_{2u} + 2\ B_{1g} + 2\ B_{2g} + 2\ B_{2u} + 2\ E_g + 5\ E_u$. Here the A_{1g}, B_{1g}, B_{2g}, and E_g species are Raman active, the A_{2u} and E_u species are infrared active, and the A_{2g} and B_{2u} species are inactive.

The potential energy V for the above model is given by

$$2V = 2V_{SVF} + f[(\Delta q_1)^2 + (\Delta q_2)^2 + (\Delta q_3)^2 + (\Delta q_4)^2 + (\Delta q_1')^2 + (\Delta q')^2 + (\Delta q_3')^2 + (\Delta q_4')^2] \quad (12)$$

where V_{SVF} is the potential energy of the $(UO_5)_\infty{}^{4-}$ chain lattice under the assumption of a simple valence force field, and f in the additional term denotes the interaction force constant of the alkali atom with the oxygen atom in the $(UO_4)_\infty{}^{2-}$ plane as shown in Figure 2(b). The other force constants concerning the interactions of the alkali atom with the oxygen atom in the endless –O–U–O–U– chain and between the chains may be neglected since such interactions are considered to be very weak in comparison with the former case.

The similar normal-coordinate treatment as foregoing interpreted was carried out on the basis of this modified force field. The force constants used on the frequency calculation are listed in Table II (set 2). The additional interaction force constants for the Li---O and Na---O bonds are estimated from Badger's

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(9) M. Tsuboi, M. Terada, and T. Shimanouchi, *J. Chem. Phys.*, **36**, 1301 (1962).

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relationship.[8] It is seen from Table II that these force constants have large values beyond expectation. The frequencies calculated on the basis of these force constants are shown in Table I. For Li_4UO_5, the addition of the interaction force constant *f* to the modified force field gives the best agreement between the observed and calculated frequencies. Furthermore, the band broadening at near 590 cm^{-1} can be well explained by the appearance of the A_{2u} (624 cm^{-1}) vibration mode (Figure 3) caused by the Li---O interaction. On the other hand, for Na_4UO_5, the agreement between observed and calculated frequencies is exact except for one (260 cm^{-1}) of the A_{2u} lattice vibrations. As in the case of Li_4UO_5, the band broadening at near 410 cm^{-1} can also be well explained by the appearance of the A_{2u} (465 cm^{-1}) vibration mode (Figure 3) caused by the Na---O interaction.

The correlation between the U–O stretching force constants and the bond distances is satisfactory in comparison with other available data[9,10] and with the results derived from Badger's relationship modified by Jones[5] and other investigators.[11,12]

It is concluded from the above treatments that the two models used here are useful not only for the interpretation of the absorption spectra of the Li_4UO_5 and Na_4UO_5 crystals but also for obtaining information on the approximate crystalline force field of such crystals.

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Mercury Species in Chloroaluminate Melts. Characterization of the New Ion Hg_3^{2+} [1a]

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Received February 19, 1971

A new ion, Hg_3^{2+}, has been obtained in acidic chloroaluminate melts (mole ratio $AlCl_3:MCl > 1$, where M is an alkali metal) by the oxidation of mercury metal, present in excess, or by the partial reduction of Hg_2^{2+}. Hg_3^{2+} has been characterized by absorption spectra, stoichiometric measurements in $AlCl_3$, and electrochemistry. The Raman spectrum of the yellow polycrystalline compound $Hg_3(AlCl_4)_2$ has been obtained and explained on the basis of the slightly bent Cl–Hg–Hg–Hg–Cl chain joined to two $AlCl_3$ groups. Equilibrium constants for the reactions $Hg^{2+} + Hg_3^{2+} = 2Hg_2^{2+}$ and $Hg_2^{2+} + Hg = Hg_3^{2+}$ are reported for several melt compositions and temperatures.

Introduction

We have previously reported[2] evidence for the existence of a new ion Hg_3^{2+} in acidic chloroaluminate melts (mole ratio $AlCl_3:MCl > 1$ where M is an alkali metal).[3] In this paper, the characterization of Hg_3^{2+} by spectral and thermodynamic data is reported.

The electrochemistry of mercury in a ternary eutectic $AlCl_3$–NaCl–KCl (66:20:14 mol %) has been previously investigated.[4–6] Gut[5] showed a polarogram indicative of an intermediate oxidation state between Hg_2^{2+} and Hg; however, no attempt was made to explain this result. Hames and Plambeck[6] concluded from polarographic and potentiometric measurements that Hg^{2+} is reduced in a conventional manner to Hg_2^{2+} and Hg. Although no electrochemical work on mercury in the melts employed in this study ($AlCl_3$–NaCl, $AlCl_3$ varied from approximately 50 to approximately 70 mol %) has been previously reported, there is no significant difference in the nature of the binary melts used in this study and the ternary melts employed previously.[4–6]

The absorption spectra of soluble mercury species in chloroaluminates have not been reported by other workers. Colored solutions were observed by Yosim and Mayer[7] in their studies of the $HgCl_2$–Hg system; the formation of colors was not attributed to a new species.

Experimental Section

The $AlCl_3$–NaCl melt was prepared from optical grade NaCl (Harshaw Chemical Co.) and $AlCl_3$ ("anhydrous and free from iron," from Fluka AG). NaCl was heated at approximately 400° under vacuum for several hours prior to use. The desired quantities of NaCl and $AlCl_3$ were weighed, placed in a quartz tube with pieces of aluminum wire (m5N grade from Alfa Inorganics), sealed under vacuum, and digested for several days at approximately 300°. After the impurities had settled, the water-clear melt was cooled slowly, frozen, and stored in a drybox (typical moisture level <2 ppm). In experiments requiring the use of $AlCl_3$ only, $AlCl_3$, prepared in the laboratory of G. P. Smith at the Oak Ridge National Laboratory using the materials and the procedure previously described,[8] was employed.

$HgCl_2$ and Hg_2Cl_2 were prepared by sublimation of AR grade materials at approximately 10^{-2} Torr. Sealed, evacuated Pyrex cells were employed for electrochemical measurements. The electrode connections were made with tungsten wire sealed in uranium glass to Pyrex. The reference electrode was an aluminum wire[8] immersed in the melt separated from the main compartment by a thin Pyrex membrane. The melt in the reference electrode compartment was either of the same composition as that in the main compartment or the melt in the reference electrode compartment was saturated with NaCl. The latter composition was employed for work at higher temperatures. Be-

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(1) (a) Research sponsored by the U. S. Atomic Energy Commission under Contract AT-(40-1)-3518 and under contract with the Union Carbide Corporation. (b) University of Tennessee. (c) On leave, University of Bari, Bari, Italy. (d) Oak Ridge National Laboratory.

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