

faults indicate terraces of about 50–100 Å. in height in the surface of the film where the stacking fault reaches the surface. It is suggested that the preferential nucleation for oxide formation at stacking faults involves the first appearance of oxide either at the re-entrant angle or the external angle of the terrace step-site. On films annealed on specimen grids and not showing stacking faults, the variation in surface density of oxide grains often is correlated with extinction contour patterns in micrographs of these films, sug-

gesting a relationship between elastic strain in the copper and nucleation of oxide grains.

In this work we have observed a definite indication of influence of the physical state of the copper on the number and location of sites which are active for the formation of cuprous oxide. The investigation is being extended to provide data for a statistical survey and to include oxidation of copper films where the physical state is altered by thermal stresses, by direct mechanical stresses, and by the incorporation of impurity atoms.

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## Uranium–Oxygen Bond Lengths in Uranyl Salts: Uranyl Fluoride and Uranyl Carbonate<sup>1</sup>

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Infrared absorption curves for carefully purified samples of  $\text{UO}_2\text{F}_2$  and  $\text{UO}_2\text{CO}_3$  have been obtained. Using the new frequencies and Badger's rule, the uranyl bond lengths are calculated as 1.71 Å. in  $\text{UO}_2\text{F}_2$  and 1.72 Å. in  $\text{UO}_2\text{CO}_3$ , in very good agreement with the Zachariasen bond length–bond strength relationship. Evidence is given to show that the U–O bond length in different uranyl salts shows relatively little variation (1.71–1.76 Å.) and that the bond order in the simple anhydrous salts may approach three.

### Introduction

The uranium coordination sphere in hexavalent uranium compounds is generally unsymmetrical, consisting of two short strong bonds to oxygen atoms situated above and below the central uranium atom and four, five, or six longer bonds distributed in or near a plane normal to the uranyl axis.<sup>2</sup> At present it is generally conceded that the O–U–O entity, the uranyl group, is linear in the solid state, and probably in solution, as well.

Unfortunately, the poor X-ray diffracting power of oxygen as compared with uranium leads to difficulties in locating the uranyl oxygen atoms with any degree of precision. In general, single crystal X-ray or neutron diffraction studies are required to provide accurate bond lengths. The good structural data which do exist clearly indicate that the uranyl bond length is not constant in the various U(VI) compounds.

Based on his X-ray studies of a number of U(VI) compounds, Zachariasen<sup>2</sup> was able to show that a single curve can be drawn to relate the uranium–oxygen bond length to its bond strength. This relationship applies to the equatorial, or secondary, oxygen atoms as well as to the uranyl, or primary, oxygen atoms. The total bond strength, as used by Zachariasen, is obtained by assuming that each atom has a bonding capability as given by its valence in the compound and that this bond strength sum is distributed over all the bonds formed by that atom. The strength of each bond

varies inversely with the bond length. A subsequent publication<sup>3</sup> provides some minor revisions in the bond length curve.

The empirical bond length–bond strength relationship has been found to give good agreement with accurate bond length measurements as they have become available and has been utilized by others to estimate uranyl bond lengths where they could not be measured accurately.

Jones<sup>4</sup> has investigated the feasibility of determining the bond lengths by infrared techniques. The uranyl ion exhibits three characteristic vibrational frequencies: the symmetric ( $\nu_1$ ) and asymmetric ( $\nu_3$ ) stretching vibrations and the bending ( $\nu_2$ ) vibration. Of these three, only the asymmetric frequency is generally observed, since the symmetric vibration should be infrared inactive for a linear  $\text{UO}_2^{+2}$  ion, and the bending frequency lies outside the range of most infrared instruments. The location of  $\nu_1$  can sometimes be determined by observation of the  $\nu_1 + \nu_3$  combination frequency. Accepted location for the vibrations are  $\nu_1 \cong 860 \text{ cm.}^{-1}$ ,  $\nu_3 \cong 930 \text{ cm.}^{-1}$ , and  $\nu_2 \cong 200 \text{ cm.}^{-1}$ , although  $\nu_1$  and  $\nu_3$  are known to appear over a substantial frequency range extending from approximately 800 to 1000  $\text{cm.}^{-1}$ .

Jones pointed out that application of Badger's<sup>5</sup> relationship (1) to force constants calculated from infrared spectra permits an evaluation of the uranyl bond length

$$R_{\text{UO}} = \beta F_{\text{UO}}^{-1/3} + d_{\text{UO}} \quad (1)$$

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) W. H. Zachariasen, *Acta Cryst.*, **7**, 795 (1954).

(3) W. H. Zachariasen and H. A. Plettinger, *ibid.*, **12**, 526 (1959).

(4) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958); *ibid.*, **11**, 409 (1958).

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

where  $R_{UO}$  is the bond length,  $F_{UO}$  is the force constant in mdynes/Å., and  $\beta$  and  $d_{UO}$  are constants whose values are determined by the bonding elements. Badger originally assumed  $\beta$  to be 1.23 for all pairs of elements but later allowed some variation in  $\beta$  depending upon the period of the bonding elements. Jones took a value of 1.08 for  $\beta$  and calculated  $d_{UO}$  at 1.17 by inserting the computed force constant (6.160 mdynes/Å.) for  $K_2UO_2F_6$  and Zachariassen's<sup>6</sup> experimentally determined value (1.76 Å.) for  $R_{UO}$  into the equation. Jones observed satisfactory agreement between the X-ray bond length ( $1.71 \pm 0.04$  Å.) for  $NaUO_2(OAc)_3$ <sup>3</sup> and the 1.73 Å. calculated from Badger's rule.

In addition to the compounds investigated by Jones, there are two anhydrous uranyl salts for which good X-ray diffraction data are available, but for which reliable infrared measurements are lacking,  $UO_2F_2$  and  $UO_2CO_3$ . Barr and Horton<sup>7</sup> have published a spectrum for uranyl fluoride, but this material is now known to have been partially hydrated. The only infrared datum on  $UO_2CO_3$  is a preliminary value of 930  $cm^{-1}$  for  $\nu_3$  reported by Jones.<sup>4</sup>

Uranyl fluoride is rhombohedral<sup>8</sup> with one molecule per unit cell. The space group is  $R\bar{3}_m$ , with  $a = 5.766 \pm 0.003$  Å.,  $\alpha = 42^\circ 47' \pm 3'$ . Zachariassen was able to measure the equatorial U-F distances accurately but not the uranyl bond lengths. He states "In the structure of  $Ca(UO_2)_2O_2$  and  $Sr(UO_2)_2O_2$  the writer found a value U-O =  $1.91 \pm 0.10$  Å. for the dimensions of the uranyl group. We shall adopt this value (for U-O in  $UO_2F_2$ )."

It should be noted that the work on  $UO_2F_2$  was completed before the bond length-bond strength curve referred to above was derived. Application of the rule to the presently accepted bond lengths gives a bond strength total of only 4.5 for uranium, instead of 6 as required by its valence. One must conclude that the relationship is not valid for  $UO_2F_2$  or that the estimated U-O distance is incorrect.

Uranyl carbonate was reported by Christ, *et al.*,<sup>9</sup> as orthorhombic. The uranyl bond length was assumed to be 1.93 Å., the secondary oxygen bond lengths were found to be  $U-2O_{II} = 2.43$  Å., and  $U-4O_{III} = 2.52$  Å. Cromer and Harper<sup>10</sup> were in agreement on most details of the  $UO_2CO_3$  structure but arrived at a U-O<sub>I</sub> distance of  $1.67 \pm 0.09$  Å. Their study with single crystals permitted determination of the uranyl bond length within the limits cited, and they pointed out the excellent agreement obtained with Zachariassen's bond strength curve.

### Experimental

A number of  $UO_2F_2$  samples were prepared from amorphous and  $\gamma$ - $UO_3$ . The amorphous trioxide was obtained from pure

$UO_2$  by reaction with 20%  $H_2O_2$ . The product  $UO_4 \cdot 2H_2O$  was filtered, dried, and then ignited to the anhydrous trioxide at  $400^\circ$  in air. The  $\gamma$ - $UO_3$  was a special reagent grade material prepared from uranyl nitrate solution by the fluidized bed process. Spectrographic analysis indicated no impurities above the parts per million level.

Two procedures were followed in the  $UO_2F_2$  preparations. (1) The anhydrous trioxide was treated with 20% HF and the product evaporated to dryness at  $50^\circ$ . This resulted in the formation of  $UO_2F_2 \cdot 2H_2O$ , which was converted to the anhydrous salt by heating at  $200^\circ$  in air. (2) The trioxide was treated with gaseous anhydrous HF at temperatures between  $350$  and  $500^\circ$  in a nickel reactor. Anhydrous uranyl fluoride is obtained directly by this procedure.

Four  $UO_2F_2$  samples prepared by these methods were analyzed for uranium and fluorine; % U found averaged 77.1% (theoretical 77.28% U), % F found averaged 12.32% (theoretical 12.33% F). The X-ray diffraction patterns from these preparations were in excellent agreement with the structure reported by Zachariassen. The presence of sharp and diffuse lines, indicative of stacking disorder, also was noted.

Uranyl carbonate was prepared by heating  $UO_3$  in water with 40 atm. of  $CO_2$  at  $105^\circ$  for 24 hr. Analysis of the product gave 13.1%  $CO_2$  (theoretical 13.32%  $CO_2$ ), and the X-ray diffraction pattern agreed with the structure reported by Cromer and Harper.

Infrared data on the uranyl salts were obtained from Nujol mulls placed between KBr plates and from KBr disks containing approximately 1% of the uranyl compounds. The spectra were determined on a Perkin-Elmer Model 421 grating spectrophotometer over the wave length range from 2.5 to 18  $\mu$  ( $4000$ - $550$   $cm^{-1}$ ).

### Results and Discussion

**Uranyl Fluoride Dihydrate.**—A broad absorption is observed in the OH stretching region with a maximum at  $3500$   $cm^{-1}$ . The uranyl absorption is of medium intensity and sharpness with a maximum at  $935$   $cm^{-1}$ .

**Anhydrous Uranyl Fluoride.**—In every instance only two peaks not attributable to Nujol are observed over the entire spectral range from  $4000$ - $550$   $cm^{-1}$ . A strong peak, whose exact location varies slightly depending upon the preparative method, is observed in the  $\nu_3$  region. The "wet" method  $UO_2F_2$  gives the absorption maximum at  $1010$   $cm^{-1}$  while the salt prepared by the "dry" method has its maximum at  $990$   $cm^{-1}$ . The peak is relatively sharp but tends to tail off slightly on the long wave length side. This effect may be due to the stacking disorder noted by Zachariassen. The second peak is the  $\nu_1 + \nu_3$  combination peak which is detectable, albeit very weakly, at  $1872$   $cm^{-1}$ .

Comparison of the hydrated and anhydrous uranyl fluoride spectra with that given by Barr and Horton suggests that their material contained a mixture of the two species.

**Uranyl Carbonate.**—In addition to the maxima attributable to the carbonate group, only one absorption peak was positively identified in the infrared. This is a strong absorption at  $965$   $cm^{-1}$ , due to the asymmetric uranyl vibration. The  $\nu_1 + \nu_3$  combination band was tentatively identified as a very weak maximum at  $1835$   $cm^{-1}$ .

As shown by Jones, identification of the asymmetric stretching ( $\nu_3$ ) and combination ( $\nu_1 + \nu_3$ ) frequencies

(6) W. H. Zachariassen, *Acta Cryst.*, **7**, 783 (1954).

(7) J. T. Barr and C. A. Horton, *J. Am. Chem. Soc.*, **74**, 4430 (1952).

(8) W. H. Zachariassen, *Acta Cryst.*, **1**, 277 (1948).

(9) C. L. Christ, J. R. Clark, and H. T. Evans, Jr., *Science*, **121**, 472 (1955).

(10) D. T. Cromer and P. E. Harper, *Acta Cryst.*, **8**, 847 (1955).

permits calculation of the bond force constant and the U-O bond distance in these compounds. If Jones' values for  $\beta$  (1.08) and  $d_{UO}$  (1.17) are used, the calculated bond force constants and bond lengths are as follows:  $UO_2F_2$ :  $F_{UO} = 7.89$  mdynes/Å.,  $R_{UO} = 1.712$  Å.  $UO_2CO_3$ :  $F_{UO} = 7.59$  mdynes/Å.,  $R_{UO} = 1.720$  Å.

The uranyl bond length calculated for  $UO_2CO_3$  is well within the limits ( $1.67 \pm 0.09$  Å.) set by Cromer and Harper in their single crystal studies. The bond length for  $UO_2F_2$  is now in accord with the empirical bond strength relationship and indicates that Zachariassen's assumed value is incorrect. The agreement between the infrared data and the bond length-bond strength rule for the two salts is now complete since the uranium bond strength totals 6 in each instance.

As has been pointed out by McGlynn,<sup>11</sup> the numerical values assigned  $\beta$  and  $d_{UO}$  may be varied to a considerable extent without jeopardizing the agreement between infrared and X-ray measurements on  $K_3UO_2F_5$  and  $NaUO_2(OAc)_3$ . Existing data<sup>12</sup> on bond lengths as a function of force constants throughout the periodic table, however, suggest that the values assigned by Jones are reasonable. The emphasis should not, however, be placed on the exact value of the constants to be inserted into the equation but rather on the conclusion that uranyl salts with asymmetric vibrational frequencies in the 850-1000  $cm^{-1}$  region will have approximately equal uranyl bond lengths. A survey of the reported infrared spectra of some 20 anhydrous, hydrated, and complex uranyl salts (in addition to those discussed in Table I) reveals that  $\nu_3$  in every instance falls within this frequency range, for which one calculates a bond length of 1.71 to 1.76 Å. The spectra of the majority of the salts listed in Table I were checked and agreement with  $\nu_3$  assignments was observed in every instance.

**Influence of Equatorial Ligands on Uranyl Bonding.**—Attempts have been made to correlate uranyl bond lengths with identity of equatorial ligands<sup>11,13</sup> on the assumption that these groups will cause changes, either in the extent of uranyl dative bonding or in the covalent-ionic character of the uranyl bonds. The infrared data given above indicate that the influence of equatorial ligands is a minor one which may be overshadowed by other effects. Thus  $UO_2F_2$  and  $K_3UO_2F_5$ , which represent the extremes in observed  $\nu_3$  frequency among uranyl salts, possess identical secondary ligands. The variation in uranyl bond length may be due to change in uranium coordination number from 8 to 7 but also can be interpreted in terms of the potassium ions. The increased U-O bond length in the double salt can be attributed to ionic O-K bonding or to a decrease in U-O dative bonding occasioned by the proximity of  $K^+$  ions to the uranyl oxygens.

McGlynn and his colleagues have reported a careful study of ligation effects by infrared measurements

(11) S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961).

(12) D. R. Herschbach and V. W. Laurie, *ibid.*, **35**, 458 (1961).

(13) G. B. Bokii and L. O. Atovmyan, *Zh. Strukt. Khim.*, **2**, 308 (1961).

TABLE I

URANYL ASYMMETRIC VIBRATIONAL FREQUENCIES IN ITS SALTS

Compound	$\nu_3$ in $cm^{-1}$ <sup>a</sup>
I. Anhydrous salts	
$UO_2SO_4$	925 <sup>b</sup>
$UO_2(OAc)_2$	940 <sup>b</sup>
$UO_2C_2O_4$	930 <sup>b</sup>
$\beta-UO_2(OH)_2$	935 <sup>c</sup>
II. Hydrated salts	
$UO_2Cl_2 \cdot 3H_2O$	900-950 <sup>b,d</sup>
$UO_2(NO_3)_2 \cdot 2H_2O$	937-952 <sup>e-h</sup>
$UO_2(NO_3)_2 \cdot 3H_2O$	943-950 <sup>f-h</sup>
$UO_2(NO_3)_2 \cdot 6H_2O$	933-964 <sup>d-h</sup>
$UO_2SO_4 \cdot 3H_2O$	913-950 <sup>d-h</sup>
$UO_2HPO_4 \cdot 4H_2O$	920 <sup>i</sup>
$UO_2(OOCH)_2 \cdot H_2O$	955, 942 <sup>d</sup>
$UO_2(OAc)_2 \cdot 2H_2O$	918-950 <sup>d,h</sup>
$UO_2C_2O_4 \cdot 3H_2O$	930-961 <sup>d,i</sup>
$UO_2(OH)_2 \cdot H_2O$	950 <sup>c</sup>
III. Double salts	
$K_2UO_2Cl_4 \cdot 2H_2O$	903 <sup>h</sup>
$KUO_2(NO_3)_3$	943-953 <sup>f,j</sup>
$CsUO_2(NO_3)_3$	956 <sup>g,j</sup>
$K_2UO_2(SO_4)_2 \cdot 2H_2O$	907-909 <sup>h,h</sup>
$(NH_4)_2UO_2(SO_4)_2 \cdot 2H_2O$	911 <sup>b</sup>

<sup>a</sup> Where more than one determination has been published, the frequencies shown correspond to the minimum and maximum reported. <sup>b</sup> J. Le Comte and R. Freymann, *Bull. soc. chim. France*, **8**, 622 (1941). <sup>c</sup> A. M. Deane, AERE-R3411 (1960). <sup>d</sup> J. H. Lady and R. E. Adams, NP-9624 (July 31, 1957). <sup>e</sup> G. L. Caldwell, A. B. Van Cleave, and R. L. Eager, *Can. J. Chem.*, **38**, 772 (1960). <sup>f</sup> J. G. Allpress and A. N. Hambly, *Australian J. Chem.*, **12**, 569 (1959). <sup>g</sup> B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, 3965 (1958). <sup>h</sup> A. N. Sevchenko and B. I. Stepanov, *Zh. Eksp. Teoret. Fiz.*, **21**, 212 (1951). <sup>i</sup> K. V. Narasimham, *Indian J. Phys.*, **34**, 321 (1960). <sup>j</sup> G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," NNES Vol. III-2, McGraw-Hill Book Co., New York, N. Y., 1949.

which indicate a variation in  $R_{UO}$  of only 0.03 Å. rather than the 0.4 Å. which had been suggested by some X-ray data.

**Bond Strength Interpretation of Uranyl Bonding.**—In spite of the fact that the bond length-bond strength curve is an empirical relationship, it does give agreement with experimentally determined bond lengths in all instances where definitive data are available and can give suitable interpretations of additional data where precise bond length measurements do not exist. The configuration of the uranyl group, with a strongly bonded oxygen atom above and below the uranium atom (bond strength  $\cong 2$ ), should result in a layer lattice, since only the equatorial ligands can participate in the formation of an infinite lattice. Differences in the electrophilic properties of the equatorial ligands, and in the secondary bonding between layers, should cause only minor variations in the uranyl bond length and in the observed vibration frequencies. The infrared data and existing accurate X-ray results ( $UO_2F_2$  and  $UO_2CO_3$ ) are in agreement with this assumption.

Hydration of uranyl salts leads to the possibility of hydrogen bonding between equatorial ligand and uranyl oxygen, thus weakening the primary U-O bond. The bond force constant and the vibrational frequency are decreased, and the bond length increased. This effect

is responsible for the observed change in  $\nu_3$  occasioned by hydration of  $\text{UO}_2\text{F}_2$ . The uranyl oxygen atoms are not necessarily involved in hydrogen bonding, *i.e.*, bonding may occur between secondary oxygen atoms in different layers of the lattice or within the same layer. In these instances one would expect little change in  $\nu_3$  and in bond length as a result of hydration. Uranyl acetate and oxalate may be examples of this situation.

Bonding between layers in uranyl salt crystals also may be accomplished by metal ions in uranyl double salts. In some instances, the second metal atom is bonded only to the equatorial ligands. In these compounds, the asymmetric stretching frequency of the double salt should not be materially changed over that observed for the simple anhydrous uranyl salt; *e.g.*, uranyl acetate and sodium uranyl acetate. In other instances atoms of the second metal are located at reasonable metal-oxygen distances for ionic bonding to the uranyl oxygen. Here a decrease in asymmetric stretching frequency and increase in U-O bond length is to be expected, *e.g.*,  $\text{UO}_2\text{F}_2$  and  $\text{K}_3\text{UO}_2\text{F}_6$ .

Dyatkina, *et al.*,<sup>14</sup> have argued that there are no grounds for assuming that part of the valency power of the O atoms of the uranyl group is used for a bond with cations of the non-coordinated sphere. However, an analysis of uranium(VI) bonding appears to corroborate the bond strength interpretation. The uranyl oxygen atoms are reported to retain some negative charge<sup>15</sup> and should participate in ionic bonding to the metal cation whenever the M-O distance approximates the ionic radius sum of the respective ions. This effect has been noted in  $\text{K}_3\text{UO}_2\text{F}_6$ ,<sup>16</sup> but is better demonstrated in the monouranates of the alkaline earth metals<sup>16</sup> and in  $\text{Na}_4\text{UO}_6$  and  $\text{Li}_4\text{UO}_6$ .<sup>17</sup>

**Bond Order vs. Bond Strength.**—A comparison (Fig. 1) of the Zachariasen bond length-bond strength curve and the force constant-bond length curve obtained from Badger's rule reveals that the two are not directly

(14) M. E. Dyatkina, V. P. Markov, I. V. Tsapkina, and Y. N. Mikhailov, *Akad. Nauk SSSR Neorgan. Khim.*, **6**, 575 (1961).

(15) R. E. Connick and Z. Z. Hugus, *J. Am. Chem. Soc.*, **74**, 6012 (1952).

(16) W. H. Zachariasen, *Acta Cryst.*, **1**, 281 (1948); *ibid.*, **7**, 788 (1954).

(17) S. Siegel and H. Hoekstra, to be published.

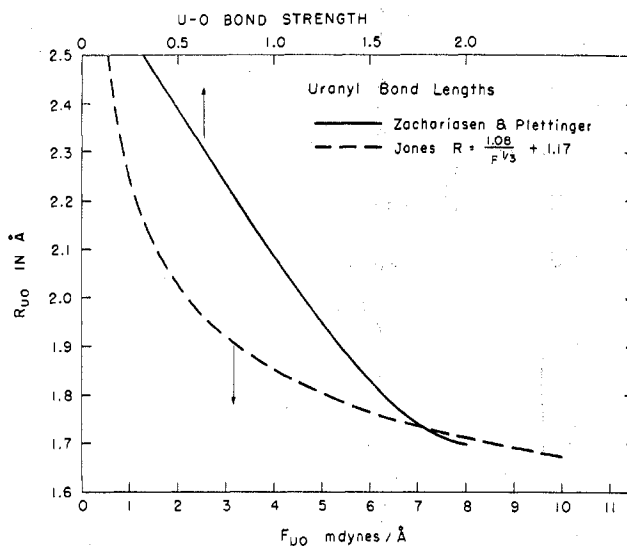


Figure 1.

related. Bond force constants have been reported to be linearly related to bond order,<sup>18</sup> but it is evident that this is not true for the bond order-bond strength relationship.

The Zachariasen curve gives a bond length of 2.08 Å for unit bond strength. Using the constants derived by Jones, one obtains a force constant of 1.70 mdynes/Å for this bond length. Relationships established between force constant and bond order agree that a covalent double bond force constant will be two to three times as great as the single bond constant. The calculated value at 1.71 Å (bond strength = 2), however, is 8.0 mdynes/Å, a ratio of 4.8 to 1. This unusually high value suggests strongly that the uranyl "double" bond corresponds to a bond order or bond multiplicity greater than two, as indicated by Dyatkina<sup>14</sup> and by McGlynn and Smith.<sup>19</sup>

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(18) G. R. Somayajulu, *J. Chem. Phys.*, **28**, 814 (1958).

(19) S. P. McGlynn and J. K. Smith, *J. Mol. Spectry*, **6**, 164 (1961).