

Spectroscopy and Photochemistry of Uranyl Compounds



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Volume 1

**SPECTROSCOPY AND PHOTOCHEMISTRY
OF URANYL COMPOUNDS**

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Spectroscopy and Photochemistry of Uranyl Compounds

by

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PREFACE

DURING the wartime development of the atom bomb in the Manhattan Project, the need arose to systematize our knowledge of the chemistry of uranium. When the project ended in 1945, a compendium of uranium chemistry, prepared by the Information Division of the Project, was about to be converted into a handbook. The first volume of this handbook, by J. J. Katz and E. Rabinowitch, appeared in 1951 as volume 5 in Division VIII of the Nuclear Energy Series, published by McGraw-Hill* and Company for the Atomic Energy Commission. This series, intended to cover all scientific research of the Manhattan Project laboratories, was never completed. The published volume of the chemistry of uranium contained a critical survey of work concerning the element uranium and its binary compounds. A second volume was intended to cover oxygen-containing uranium salts and their solutions, in particular the uranyl compounds. A part of this volume, prepared by E. Rabinowitch and dealing with spectroscopy, fluorescence and photochemistry of uranyl compounds, was circulated in the form of four AEC reports.† Later, the Pergamon Press suggested its publication as a monograph. Professor Belford of the University of Illinois agreed to bring the text up to date by including research carried out in the fifteen years since the writing of the original text. He also added a chapter on the electronic structure of the uranyl ion, including his own work in this field.

The authors believe that the volume will satisfy a real need of researchers in the chemistry and physics of the actinide elements. The uranyl ion is probably the best-known chemical entity in the actinide series. It has been studied for over a century and a half. The fluorescence and photochemical sensitivity of uranyl compounds has attracted early attention; hundreds of research papers exist in this field. Yet many basic experimental questions remain unsettled,

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† ANL 5122, 5173, 5291 and 5202.

and a theory of the uranyl ion explaining its spectroscopic behaviour is only rudimentary.

Examination of the literature suggests that many now active researchers had not made sufficient use of previously reported work. This shortcoming is inevitable in the time when research is rapidly expanding; it can be somewhat alleviated by a comprehensive guide to past work. Our aim was to provide such a guide. We have endeavored to present the material in such a manner that the book should be continually useful for many years, providing it is kept up to date by the reader by his own literature scanning. To this end, the presentation within each subchapter is largely chronological; the work of each researcher is clearly attributed, and conclusions are frankly labeled as his own. This presentation may make for choppy reading, but it seemed preferable to a "unified" treatment that would convey the false impression of a well-understood and neatly ordered field, and would soon become obsolete.

Undoubtedly there is some pertinent material in the literature which we have not cited. For example, there are many references to absorption spectra of uranyl complexes in the literature on analytical chemistry, and many reports exist dealing with uranyl oxalate actinometry, to which we have not referred. Further, coverage from 1960 to date is sparse.

This book owes much to the monograph "Spectroscopic Properties of Uranium Compounds" by G. H. Dieke and A. B. F. Duncan* which summarized the studies carried out by these researchers at the Johns Hopkins University under the Manhattan Project program during the war.

E. I. RABINOWITCH
R. L. BELFORD

* See Bibliography

CHAPTER 1

SPECTROSCOPY OF URANYL SALTS IN THE SOLID STATE

1. Introduction. Qualitative Interpretation of the Uranyl Spectrum

THE divalent uranyl ion, UO_2^{++} , can be considered as an intermediate product of hydrolysis of the ion $\text{U}^{+6} + 4\text{OH}^- \rightarrow \text{UO}_2^{++} + 2\text{H}_2\text{O}$; an intermediate, however, that possesses a remarkably wide range of stability. The absorption and fluorescence bands of most solid or dissolved uranyl salts in the visible and near-ultraviolet belong to this ion, and are therefore similar in their general pattern, except for minor changes in position, width, and intensity of the individual bands caused by the electrical fields of the surrounding anions (in crystals or ionic complexes), or water dipoles (in crystal hydrates or aqueous solutions).

In addition to the absorption and emission bands due to electronic excitation within the uranyl ion, uranyl compounds could have also spectral bands due to excitation of the associated anions (or molecules), or to the transfer of electrons from these anions or molecules to the uranyl ions ("electron affinity," or—more correctly—"electron transfer" spectra). With the exception of salts of colored anions (such as chromate), the electronic bands of the last-named types lie, however, at much shorter waves than the absorption bands due to excitation of low-lying electronic levels within the uranyl ion itself.

In absorption, most solid or dissolved uranyl salts show a regular sequence of broad bands (or rather, band groups, as revealed by their resolution into narrow bands or "lines" at low temperatures) covering the blue, violet, and near-ultraviolet region; in fluorescence, a similar sequence extends from the blue into the green and yellow part of the spectrum. To interpret the spectra in detail demands structural information about the individual salts.

2 Spectroscopy and Photochemistry of Uranyl Compounds

1.1. Structure of Uranyl Crystals

X-ray diffraction studies have yielded some information regarding the geometry of uranyl salts. No crystal data have yet shown a bent structure for the ion $(\text{O—U—O})^{++}$ [Zachariasen (1954c)]. Instead,

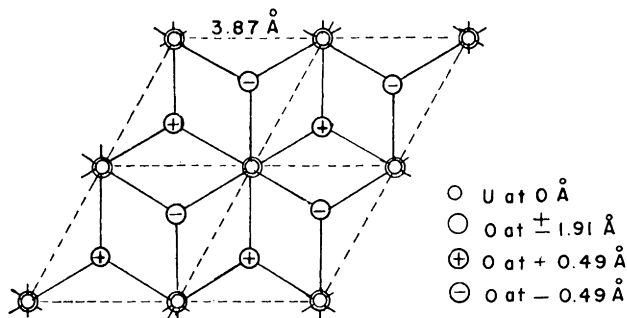


FIG. 1.1. Structure of a layer of $\text{UO}_2.\text{O}_2$ in CaUO_4 . After Zachariasen (1948b).

all investigated salts were found to contain a symmetric, linear $(\text{OUO})^{++}$ ion, surrounded by atoms forming secondary U-ligand linkages considerably longer than the primary U—O distance in

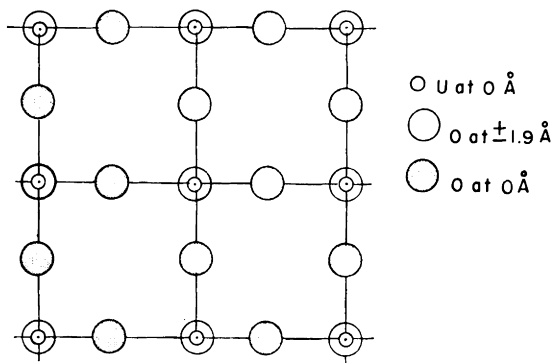


FIG. 1.2. Probable structure of a layer of $\text{UO}_2.\text{O}_2$ in BaUO_4 . After Zachariasen (1948) and Samson and Sillén (1947).

$(\text{OUO})^{++}$. The first demonstration of this configuration was by Fankuchen (1935); however, he obtained no reliable bond distances.

Zachariasen (1948b) examined $(\text{UO}_2)_2\text{O}_2\text{Ca}$ and $(\text{UO}_2)_2\text{O}_2\text{Sr}$. These “orthouranates” consist of sheets containing linear O—U—O

groups, directed perpendicular to the sheet plane and having primary U—O bonds of 1.91 ± 0.10 Å, and secondary O atoms at 2.30 Å from the U atoms, arranged as shown in Fig. 1.1. The Ca^{++} or Sr^{++} ions bind the uranate layers together.

Another orthouranate, BaUO_2O_2 , is not isostructural with the Ca and Sr compounds, and according to the X-ray analysis of Samson and Sillén (1947) each uranyl ion has only four secondary U—O

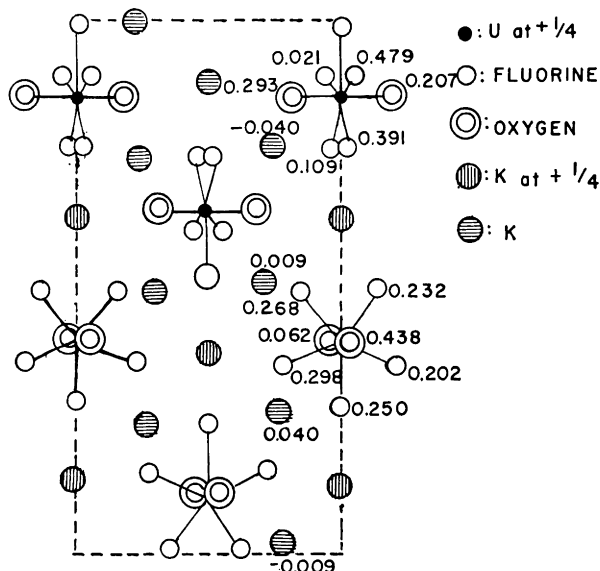


FIG. 1.3. Structure of $\text{K}_3\text{UO}_2\text{F}_6$, according to Zachariasen. Coordinate of some atoms above plane of projection is shown on the diagram. Each UO_2 is surrounded by 5 F, spaced uniformly on the equatorial circle of radius 2.24 ± 0.3 Å. The shortest $\text{K}^+ - \text{F}^-$ distance is 2.54 Å; the shortest K—O distance is 2.92 Å.

bonds. The structure proposed by Samson and Sillén is shown in Fig. 1.2. According to Frondel and Barnes (1958), there is a PbUO_2O_2 isostructural with the Ba compound.

Other uranyl salts are structurally similar to these oxides. Zachariasen (1948a) found that anhydrous UO_2F_2 crystallizes in sheets, each sheet having a structure like the UO_2O_2^- layers in calcium uranate (see Fig. 1.1). However, the UO_2F_2 layer is slightly more expanded than the UO_2O_2^- layer. Corresponding distances

are: U—U = 3.87 Å in the uranate, 4.20 Å in the fluoride; U—O (secondary) = 2.3 Å in the uranate, U—F = 2.5 Å in the fluoride.

The few structural studies of uranyl salts which have been made have revealed a variety of U—O primary bond lengths. Zachariasen (1954a) found that in $K_3UO_2F_5$ crystals, the $UO_2F_5^{-3}$ group is a pentagonal bipyramid with the U—O distance = 1.76 ± 0.03 Å, and the U—F distance = 2.24 ± 0.02 Å. Thus the uranyl ion is considerably shorter in this salt than it is in the orthouranates. More accurate data by Zachariasen (1954b) on a different uranate, $MgUO_2O_2$, has given the U—O primary distance as 1.91 ± 0.03 Å. This salt contains

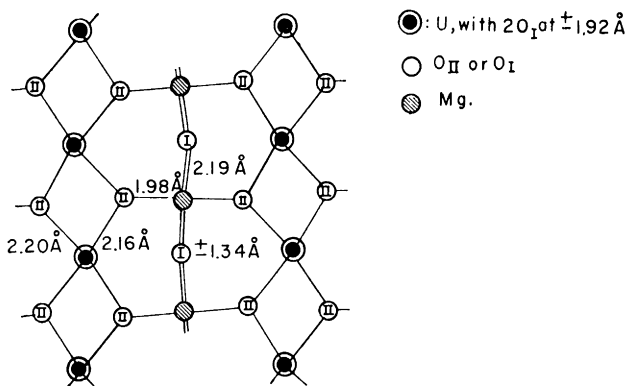


FIG. 1.4. A diagram of the $MgUO_2O_2$ structure as given by Zachariasen (1954b). This seems to be a compound of $(OMgO).(OUO)$, with the oxygens attached to each metal ion forming secondary bonds with another one to give each 4 equatorial ligands.

endless chains of UO_2O_2 groups, with six O atoms from four chains forming octahedra about the Mg^{++} ions. The four secondary U · · O bonds are reported as 2.18 ± 0.04 Å (not necessarily all equal). These structures are pictured in Figs. 1.3 and 1.4.

The compounds $RbUO_2(NO_3)_3$ and UO_2CO_3 complete the group of uranyl salts for which we have a fair degree of detailed X-ray structure information. They are similar in that each involves uranyl groups surrounded by a planar arrangement of six NO_3^- or CO_3^{--} oxygens. The nitrate was studied by Hoarde and Stroupe (1949), who placed only the U atoms by intensity considerations, and the rest by a combination of bond-length guesses and symmetry considerations. A similar procedure was followed for the carbonate by

Christ, Clark, and Evans (1955). Their sample was the natural mineral Rutherfordine. However, Cromer and Harper (1955), using a synthesized carbonate sample, augmented the work of Christ *et al.* by an intensity placement of the uranyl oxygens at $1.67 \pm 0.09 \text{ \AA}$ from U. The work of these groups gives a structure as shown in Fig. 1.5, with 6 $\text{U}-\text{O}_{\text{II}}$ distances of about $2.5 \text{ \AA}$.

Zachariasen (1954c) has given an interesting rationale for the apparent wide variation in the uranyl bond length among various salts. His discussion is based on variations in "bond strength," but it amounts to a suggestion that the uranyl bond will be longer if its oxygen atoms are shared with other external atoms. It is quite clear that the coordination number of uranium in uranyl can vary at least

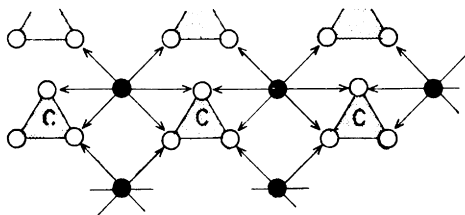


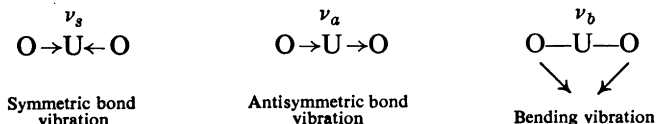
FIG. 1.5. Sketch of the plane of the carbonate groups in uranyl carbonate. Adapted from Christ, Clark and Evans (1955). Carbonate groups shown as shaded triangles; uranium atoms as black circles.

from 4 to 6 (we do not include the uranyl linkages in counting coordination), and very likely coordination with 8 or more ligands can also occur. Moreover, for a given coordination number, the ligand arrangement is not fixed. For example, the six ligand oxygens in CaUO_2O_2 (Fig. 1.1) surround the UO_2 in two equilateral triangles, one above and one below the equatorial plane, while the six ligand oxygens of UO_2CO_3 form a (distorted) hexagon in the equatorial plane. This, together with the relative constancy of geometry of the uranyl group itself, suggest that strong directed-valence bonds join the uranyl atoms but that electrostatic forces and packing conditions play the important roles in secondary U-ligand bonds. (This does not, however, imply that directed covalency does not occur in these secondary bonds.) We note in passing that there is no simple correlation between the coordination number of the U and the uranyl bond length.

It seems reasonable to discuss spectra as arising from the uranyl group with specific secondary ligand and lattice interactions.

1.2. General View of Uranyl Crystal Spectra

A linear OUO^{++} group has three fundamental vibrations:



The bending vibration, ν_b , is degenerate (since it can occur in two mutually perpendicular planes); it should therefore split into two components when the ion is placed into an external field of force (except when this field is directed along the O—U—O axis). The excitation of the symmetric vibration, ν_s , has no dipole moment change associated with it, and should therefore be absent from the infrared absorption spectrum. In the Raman spectrum, inversely, *only* the symmetric vibration, ν_s , should occur. All three vibrations are permitted in combination with changes in electronic structure, i.e. in visible and ultraviolet absorption and emission bands.

These expectations are not confirmed by experience: the frequency 860 cm^{-1} , which should be ν_s in the linear model (cf. p. 28), is represented—albeit weakly—also in the infrared absorption spectrum, and the frequency of $\sim 210\text{ cm}^{-1}$, corresponding to ν_b in the linear model, is present, with moderate intensity, in the Raman spectrum of uranyl salt solutions.

The exclusion rules for the infrared and Raman spectrum are, however, strictly valid only for *free* molecules (or molecular ions), while what is observed in practice are the spectra of uranyl ions in the electric field of anions, other ligands, or solvent dipoles. Under these conditions, “prohibited” transitions are not impossible, although they remain comparatively improbable and can be expected to give rise to lines which are weaker than those due to permitted transitions.

An alternative explanation—that the ion UO_2^{++} is angular—has been advanced, specifically in application to solutions (to avoid contradiction with X-ray data which definitely indicate linear structure in crystals). However, at present it seems most likely that the ion UO_2^{++} remains linear also in the solvated state, but that

solvation weakens the exclusion rules for the Raman spectrum so as to bring out the ν_b frequency.

If the three vibrations are assumed to be harmonic, with the elastic force constants f (in the direction of the U—O bond) and d (in the direction perpendicular to this bond), their frequencies must be:

$$\nu_s (\text{symmetric}) = \sqrt{\left(\frac{f}{m_o}\right)} \quad (1)$$

$$\nu_a (\text{antisymmetric}) = \sqrt{\left[\frac{f}{m_o} \left(1 + \frac{2m_o}{m_u}\right)\right]} = \nu_s \sqrt{\left(1 + \frac{2m_o}{m_u}\right)} \quad (2)$$

$$\nu_b (\text{bending}) = \sqrt{\left[\frac{2d}{f} \left(1 + \frac{2m_o}{m_u}\right)\right]} = \nu_a \sqrt{\frac{2d}{f}} \quad (3)$$

where m_o and m_u are the masses of the atoms of oxygen and uranium respectively.

Since $m_u \simeq 15 m_o$, the antisymmetric vibration frequency must be about 6 per cent higher than the symmetric one. The bending frequency, on the other hand, can be expected to be considerably lower than the other two fundamental frequencies (because of the relation $d \ll f$). We will see below that the values of ν_s and ν_a for uranyl salts (in the stable electronic state) are about 880 and 920 cm^{-1} respectively, while ν_b appears to be of the order of 200 cm^{-1} (although the identification of this vibration is not yet quite certain).

The existence of two fundamental frequencies, ν_s and ν_a , of approximately equal magnitude, could lead to a spectrum of considerable complexity; instead, the absorption spectra (and to an even greater extent, the fluorescence spectra) of uranyl compounds appear to be rather simple, consisting of a single series of approximately equidistant band groups. This indicates that only one type of vibration is so strongly coupled with the electronic transition that several quanta of this vibration (up to 8, as indicated by the number of band groups in the spectrum) can be excited in conjunction with this transition. We will see below that this is the symmetric bond vibration. Of the antisymmetric and the bending vibration, on the other hand, apparently not more than one quantum can be excited in conjunction with the transition from the lowest excited electronic state to the ground state (which gives rise to the fluorescence spectrum at low temperatures). In the reverse transition—from

the ground electronic state to the excited electronic state—one or two quanta of the vibrations ν_a^* and ν_b^* can be excited (asterisks denote the excited electronic state). A further complication arises in the absorption spectrum from the fact that apparently not one but several electronic states of the UO_2^{2+} ion can be reached by the absorption of visible or near-ultraviolet light, while only the lowest one of these states contributes to fluorescence.

That the one vibration strongly coupled with the electronic transition, must be the symmetric bond vibration, ν_s , follows from the Franck–Condon principle. According to the latter, the electronic transition is so fast that it leaves the nuclei in the positions and with the velocities close to those they had before the transition; if the molecule in the new electronic state cannot have these co-ordinates without a change in the number of vibrational quanta, the acquisition (or loss) of these quanta will follow the electronic transition. In the case of the symmetric bond vibration in the linear O—U—O system, such a change is to be expected, because electronic excitation changes the strength of the U—O bond, and thus also the U—O distance of minimum potential energy.

If, as is likely, the equilibrium distance is wider in the electronically excited state than in the ground state, the oxygen atoms will find themselves, after the emission of a quantum of fluorescent light, too far apart and the system will begin to vibrate like a stretched and released spring.

At first one may think that the same consideration should apply also to the antisymmetric vibration; but while in the case of the symmetric bond vibration, the excess potential energy of the stretched O—U—O system is decreased when two oxygen atoms move simultaneously towards the U atom, no similar approach to equilibrium is possible by the excitation of the antisymmetric vibration, since in it the two oxygen atoms move in the same direction—one toward the uranium atom, and the other away from it. Therefore, in the first approximation (i.e. assuming an elastic force), antisymmetric vibrations should not be excited at all as a consequence of electronic transition; the actually observed excitation of a single quantum of this vibration in fluorescence must be attributed to deviation of the bond from elasticity. This deviation appears to be stronger in the excited electronic state, since two quanta of antisymmetric vibration can be acquired in absorption.

The bending vibration, ν_b , is also relatively little affected by the excitation of one of the bonding electrons in the O—U—O system. A much stronger excitation of this vibration could be expected if the uranyl ion were non-linear in the excited electronic state.

To sum up, the (low-temperature) *fluorescence spectrum* of the uranyl ion can be represented by the equation:

$$\nu_{fl} = \nu_F - n_s \nu_s - n_a \nu_a - n_b \nu_b - \sum n_i \nu_i \quad (4)$$

where ν_F is the pure electronic transition ("resonance transition"), and n_s ($= 0$ to 8) the number of quanta of the symmetric vibration excited simultaneously with the loss of the electronic quantum, $h\nu_F$. The coefficients n_a and n_b are either 0 or 1 . The term $\sum n_i \nu_i$ refers to vibrations of the associated anions (such as NO_3^-), water molecules, or the crystal as a whole, which too can be coupled with the electronic transition—either directly or, more likely, through the intermediary of the fundamental vibrations in the O—U—O system. The low-temperature *absorption spectrum* of the uranyl ion can be similarly represented by the equation:

$$\nu_{\text{abs}} = \nu_E + n_s \nu_s^* + n_a \nu_a^* + n_b \nu_b^* + \sum n_i \nu_i \quad (5)$$

where ν_E can be equal either to ν_F or to the excitation frequency of some higher electronic term of the UO_2^{++} ion. In this case, too, $n_s = 0$ to 8 , and n_a and n_b can have the values 0 , 1 or 2 .

Figures 1.6A and 1.6B are simplified term schemes of the low-temperature fluorescence and absorption spectra of the uranyl ion respectively. Each arrow corresponds to a band group with a common value of n_s . A second electronic level, M , is indicated in Fig. 1.6B in addition to the lowest level, F , in which the low-temperature fluorescence spectrum originates.

The sub-levels due to the vibrational frequencies ν_a and ν_b are not shown in Fig. 1.6. Because the frequency ν_a is $\simeq \nu_s$, the absorption bands $\nu_E + n\nu_s + \nu_a$ will be located among the bands of the group $\nu_E + (n+1)\nu_s$; the fluorescence bands among those of the group $\nu_F - (n+1)\nu_s$. Thus, the *empirical* definition of a band group as comprising bands situated close together (and fusing into a single, broad band at higher temperatures), does not quite correspond to the *theoretical* definition, based on equations (4) and (5), according