

# Direct Evidence of Uranium(V) Intermediates by Electron Spin Resonance in Photo- and Electrolytic Reduction Processes of Uranyl Complexes in Organic Solutions

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ESR of pentavalent uranium has been observed in both processes of photo- and electrolytic-reduction of  $\text{UO}_2(\text{dimethylformamide})_5(\text{ClO}_4)_2$  in dimethylformamide. The ESR spectra are nearly symmetric. This means the case of  $g$ -factor in an axial symmetry with  $g_{\perp} > g_{\parallel}$ . Taking the values of  $g_{\perp} = 2.5$  observed and  $g_{\parallel} \sim 0$  and a usual value of  $1900 \text{ cm}^{-1}$  of spin-orbit coupling constant for uranium(V), the result of ESR is analyzed along with the experimental values of electronic spectra from visible to near infrared. Based on crystalline field theory,  $\text{U(V)}$  species in the present solution have ligands held more tightly in the equatorial plane than in the axial direction and not a form of  $\text{UO}_2^+$ , as expected.

## Introduction

Pentavalent uranium provides a deeper understanding of 5f electron behavior in actinide complexes, owing to its simple electronic configuration of  $[\text{Rn}]5f^1$ . Nevertheless there have been only a few studies of pentavalent uranium complexes, because of difficulties in preparing these complexes and their great instability. Especially in solution,  $\text{U(V)}$  is very unstable due to its thermodynamic instability with respect to disproportionation to  $\text{U(IV)}$  and  $\text{U(VI)}$ . Recently the appearance of pentavalent uranium has indirectly been suggested by an analysis of photochemical- or electrolytic-reduction processes of uranyl complexes in solution [1–3].

In the present study we observed the electron spin resonance spectra of uranium(V) and obtained a direct evidence of an existence of uranium(V) species on the way of both the photo- and electrolytic-reductions of pentakis(N,N-dimethylformamide)-dioxouranium(VI) perchlorate,  $\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$ , in DMF solution.

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## Experimental

### Materials

$\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$  was prepared by the method described previously [4]. Dimethylformamide and tetra-n-butyl-ammoniumperchlorate (TBAP) used as a supporting electrolyte were of reagent grade purity and were used without further purification. Nitrogen gas for sample preparation had a purity of 99.999%. In order to check whether or not the DMF solution of paramagnetic uranium(IV) shows the ESR absorption spectrum, we prepared  $\text{UCl}_4 \cdot 2.5\text{dmf}$  [5].

### Photochemical Reduction

Crystalline  $\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$  was dissolved under nitrogen atmosphere in DMF dried by a molecular sieve before use, and the solution was degassed by three or four freeze-pump-thaw cycles. The quartz tube containing the solution was sealed after filling with nitrogen gas. The solution was irradiated by a 500 W high-pressure mercury lamp at room temperature, and ESR spectra were recorded on a JESME-2X spectrometer at liquid nitrogen temperature.

### Electrochemical Reduction

The reaction by electrolytic reduction was performed in a simple two-electrode cell specially designed for low temperature electron spin resonance measurements [6]. The solution was prepared by dissolving a given amount of  $\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$  and TBAP into DMF in a dry box filled with nitrogen gas and degassed by the freeze-pump-thaw cycles, and then closed after filling with  $\text{N}_2$  gas. The electrolytic reduction was performed at room temperature and ESR spectra were recorded at  $-120^\circ\text{C}$ .

### Spectroscopic Measurements

Absorption spectra in a region from visible to near infrared were recorded on a EPS-3T autospectrophotometer at room temperature, to follow the change of spectra according to the reduction process.

## Results

### Optical Spectra

Optical spectra of the solution changed with the irradiation time with respect to the absorption peaks and intensities. Before the irradiation any absorption peaks were not observed in the present region of wavelength (600 ~ 1600 nm). As shown in Fig. 1a, absorptions at 770, 990 and 1480 nm appeared at the beginning of irradiation. These peaks grew with further irradiation, accompanying simultaneously the appearance of absorption peaks at 660 and 1090 nm (see Fig. 1b and c). When hydrogen perchloric acid was added to the solution showing these five peaks, three absorption peaks at 770, 990 and 1480 nm disappeared and the remainder at 660 and 1090 nm increased in intensity (see Fig. 2). This fact indicates a disproportionation reaction occurring under an existence of acid and giving rise simultaneously to the disappearance of pentavalent uranium species and the disappearance of tetravalent uranium species. Therefore, the three peaks at 770, 990 and 1480 nm can be attributed to uranium(V) and the other peaks at 660 and 1090 nm to uranium(IV). The absorption at about 1400 ~ 1600 nm is due to perchloric acid. When the irradiation continued further, the color of the solu-

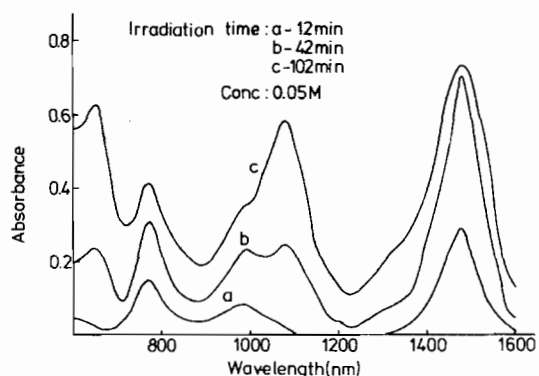


Fig. 1. Changes of absorption spectra in visible-near infrared with irradiation times.

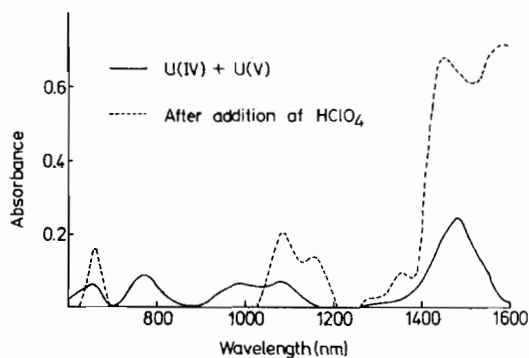


Fig. 2. Effect of addition of  $\text{HClO}_4$  on electronic absorption spectra.

tion became dark and the solution changed to a sol state showing a formation of polynuclear complexes of uranium(IV) [7, 8]. If the solution was kept in the dark, the uranium(V) species was stable for at least two weeks.

### ESR Spectra

ESR spectra were very broad, having a line-width of about 1500 gauss and nearly symmetric, as shown in Fig. 3. The value of the g-factor was about 2.5. The broad lines have also been observed on  $\text{UCl}_5$  [9] and  $\text{UCl}_5 \cdot \text{trichloroacrylylchloride}$  [10]. The intensity of spectra increased with the irradiation time. When this solution was kept in the dark at room temperature for one week, the intensity became weaker. When this solution was re-irradiated, the intensity increased again (see Fig. 4). After keeping the solu-

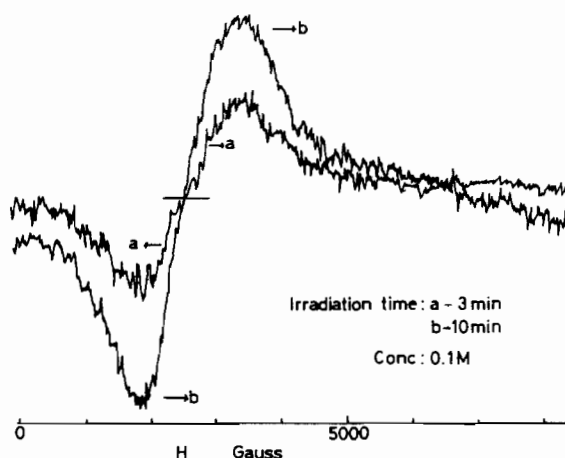


Fig. 3. ESR spectra of U(V) species in solution produced in photoreduction.

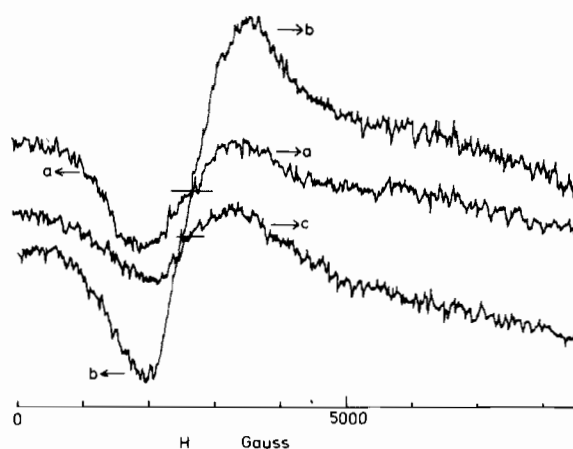


Fig. 4a and 4b. ESR spectra of U(V) species in solution kept in the dark one week after photo-irradiation. Re-irradiation times: a - - - 0 min and b - - - 16 min. 4c. ESR spectrum of U(V) species in solution (0.05 M U) reduced electrolytically with  $70 \mu\text{A}$  in 30 min.

tion for more than one week, no more spectra were observed and a dark suspension, probably an uranium hydroxide, was recognized while the color of the liquid part of the solution remained yellow. No spectrum could be observed when the ESR measurement was tried on the paramagnetic DMF solution of  $\text{UCl}_4 \cdot 2.5\text{dmf}$ .

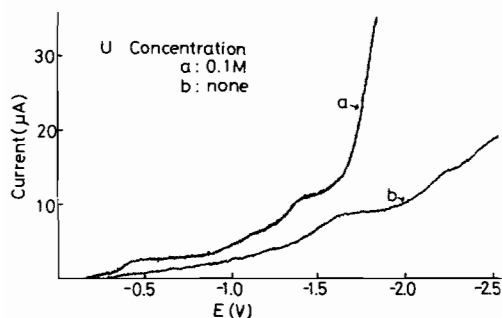


Fig. 5. Current-voltage curves of the solution to be measured and a similar solution without  $\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$ .

### Electrolytic Reduction

As shown in Fig. 5, the current-voltage curves of the sample solution and of the solution without  $\text{UO}_2(\text{dmf})_5(\text{ClO}_4)_2$  were obtained initially. Then the applying voltage to the working electrode at which the uranyl ion was reduced to uranium(V) by the cathode reaction was determined to be  $-2.0$  v. The half-wave potential of the reduction of the uranyl ion to uranium(V) was polarographically determined as  $-0.54$  v relative to a saturated calomel electrode [11]. For the two-electrode cell in the low temperature ESR measurement in the present study the linear relationship between the half-wave potential and the applied potential,  $V_a$ , at which ESR spectra of the reduced species can be detected, can be given empirically as

$$V_a = (1.92 + 0.06)E_{1/2}.$$

Therefore, the value of  $-2.0$  v of this DMF solution seems reasonable.

The appearance of uranium(V) species in the photoreduction was further confirmed by ESR measurements of this complex generated during the electrolytic reduction process. The spectrum, as shown in Fig. 4c, is similar to those of the photoreduction process. The change of spectra with the electrolytic reduction time clearly corresponded to that in the photoreduction process, and optical spectra also showed the time changes corresponding to those in the photoreduction.

### Discussion

The uranium(V) has a  $5f^1$  configuration and is iso-electronic with neptunium(VI). It seems reasonable

that uranium(V) produced by the reduction of the uranyl ion,  $\text{UO}_2^{2+}$ , has an analogous structure to the neptunyl ion,  $\text{NpO}_2^{2+}$ , where an axial field is predominant on neptunium(VI) [12]. Therefore we tried to analyze the result of ESR together with the electronic spectra, assuming the axial crystalline field around the uranium(V) as the first approximation. Under the crystalline field with the axial symmetry and spin-orbit coupling interaction, seven Kramers doublets come from splitting of the  $5f^1$  level as listed in Table I [13]. The values of g-factor can be obtained as functions of  $\theta_i$ , defined as functions of crystalline field parameters,  $\Delta$ ,  $\Theta$ , and  $\phi$  and spin-orbit coupling constant,  $\zeta$ :

$$\cot \theta_1 = \frac{(\frac{1}{2}\zeta + \phi)}{2\sqrt{3}\zeta} \pm \frac{1}{2} \sqrt{\left(\frac{\frac{1}{2}\zeta + \phi}{\sqrt{3}\zeta}\right)^2 + 4}$$

$$\cot \theta_2 = \frac{(\frac{3}{2}\zeta + \Theta)}{2 \times \frac{\sqrt{10}}{2}\zeta} \pm \frac{1}{2} \sqrt{\left(\frac{\frac{3}{2}\zeta + \Theta}{\frac{\sqrt{10}}{2}\zeta}\right)^2 + 4}$$

$$\cot \theta_3 = \frac{(\frac{5}{2}\zeta + \Delta)}{2 \times \frac{\sqrt{6}}{2}\zeta} \pm \frac{1}{2} \sqrt{\left(\frac{\frac{5}{2}\zeta + \Delta}{\frac{\sqrt{6}}{2}\zeta}\right)^2 + 4}.$$

Taking the observed g-value of about 2.5 and the three optical absorption peaks at 770, 990 and 1480 nm into account, a numerical analysis was performed to get the best fit.

In the first case, assuming the observed g-value of about 2.5 to be the value of  $g_{\parallel}$ , one of the two doublets  $|\pm \frac{3}{2}\rangle$  has a possibility of the lowest Kramers doublet and the other five doublets have not this possibility, as seen from Table I. In Fig. 6 the usual value of the spin-orbit coupling constant of U(V),  $1740 \text{ cm}^{-1}$ , is used. The electronic spectra also agree well with the experimental ones. The fact that the component of  $|0\rangle$  of the orbital angular momentum is the highest means stronger bond between uranium and oxygen in the axial direction than in an equatorial plane.

In the second case, we assume the value of  $g_{\perp}$  to be about 2.5. In this case, one of the two doublets  $|\pm \frac{1}{2}\rangle$  in Table I can be the lowest doublet. Figure 7 shows the obtained energy level diagram, where  $g_{\perp} = 2.48$  and  $g_{\parallel} = 0.23$  and the values of  $\zeta$ ,  $1900 \text{ cm}^{-1}$ , is an acceptable value for uranium(V) species. Contrary to the first case, the component of  $|0\rangle$  of the orbital angular momentum is the lowest. This indicates the stronger bond between uranium and oxygen in the equatorial plane than in the axial direction.

When we take the following facts into account:

(1) the ESR spectra were observed at the magnetic field corresponding to g-value of about 2.5, and (2) the ESR spectra corresponding to  $g_{\parallel} \lesssim 0.23$  cannot

TABLE I. Splitting Scheme of Energy Level of  $5f^1$  under Axial Crystalline Field and Spin-orbit Coupling Interaction along with Wavefunctions Obtained and Values of  $g_{\parallel}$  and  $g_{\perp}$  Calculated.

free ion + cryst. field + spin-orbit	eigenfunction	$g_{\parallel}$	$g_{\perp}$
$ m_1\rangle$ $ \pm 3\rangle$	$\cos\theta_3 2, \alpha\rangle + \sin\theta_3 3, \beta\rangle$ $\cos\theta_3 -2, \beta\rangle + \sin\theta_3 -3, \alpha\rangle$	$2(2 + \cos^2\theta_3)$	0
$ \pm 2\rangle$	$ 3, \alpha\rangle$ $ -3, \beta\rangle$	8	0
$ \pm 2\rangle$ $ \pm 5/2\rangle$	$\cos\theta_2 1, \alpha\rangle + \sin\theta_2 2, \beta\rangle$ $\cos\theta_2 -1, \beta\rangle + \sin\theta_2 -2, \alpha\rangle$	$2(1 + \cos^2\theta_2)$	0
$ \pm 1\rangle$ $ \pm 3/2\rangle$	$\sin\theta_3 2, \alpha\rangle - \cos\theta_3 3, \beta\rangle$ $\sin\theta_3 -2, \beta\rangle - \cos\theta_3 -3, \alpha\rangle$	$2(2 + \sin^2\theta_3)$	0
$ \pm 1\rangle$ $ \pm 3/2\rangle$	$\sin\theta_1 1, \beta\rangle + \cos\theta_1 0, \alpha\rangle$ $\sin\theta_1 -1, \alpha\rangle + \cos\theta_1 0, \beta\rangle$	$2\cos^2\theta_1$	$4\sqrt{3}\sin\theta_1\cos\theta_1$ $+ 2\cos^2\theta_1$
$ \pm 1\rangle$ $ \pm 3/2\rangle$	$\sin\theta_2 1, \alpha\rangle - \cos\theta_2 2, \beta\rangle$ $\sin\theta_2 -1, \beta\rangle - \cos\theta_2 -2, \alpha\rangle$	$2(1 + \sin^2\theta_2)$	0
$ 0\rangle$ $ \pm 1/2\rangle$	$-\cos\theta_1 1, \beta\rangle + \sin\theta_1 0, \alpha\rangle$ $-\cos\theta_1 -1, \alpha\rangle + \sin\theta_1 0, \beta\rangle$	$2\sin^2\theta_1$	$-4\sqrt{3}\sin\theta_1\cos\theta_1$ $+ 2\sin^2\theta_1$

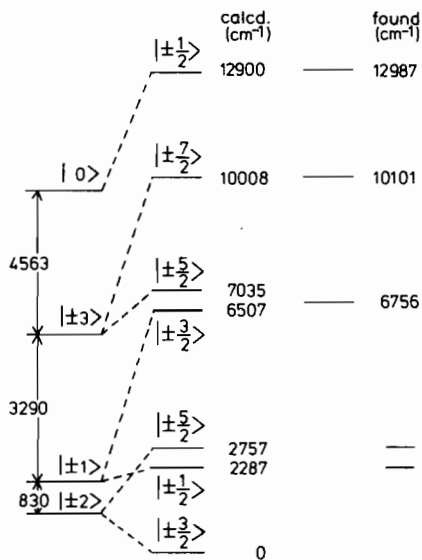


Fig. 6. Comparison of calculated energy level scheme with experimental values of electronic absorption spectra (in case of assumption,  $g_{\parallel} = 2.5$ ).

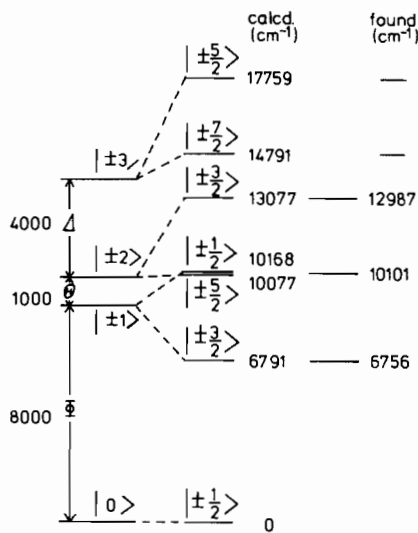


Fig. 7. Comparison of calculated energy level scheme with experimental values of electronic absorption spectra (in case of assumption,  $g_{\perp} = 2.5$ ).

actually be observed by the present ESR apparatus, both the first and second cases can be acceptable. But the nearly symmetric ESR line shape at  $g = 2.5$  can be satisfied only in the second case, where  $g_{xx} = g_{yy} = g_{\perp}$ . Therefore  $|\pm 1/2\rangle$ , originated from the  $|0\rangle$  component of the orbital angular momentum, is reasonably

interpreted as the ground state. Such a situation that  $|\pm 1/2\rangle$  is the ground state is probably the first case as far as we can be aware. This is supported by the ESR observation on  $\text{NpO}_2^{2+}$  in  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  and  $\text{CsUO}_2(\text{NO}_3)_3$  [14]: for  $\text{NpO}_2^{2+}$  in  $\text{Cs}_2\text{UO}_2\text{Cl}_4$  the ground state wave function has a large part of a  $|\pm 1/2\rangle$  state and for that in  $\text{CsUO}_2(\text{NO}_3)_3$  the important part of

the wave function is  $|\pm \frac{5}{2}\rangle$  state. Concerning the structure around the uranium(V) in the crystal, we have recently observed by a neutron diffraction analysis of  $\text{NaUO}_3$  that the octahedron of oxygen atoms around U(V) is relatively prolonged in the direction perpendicular to the equatorial plane [15].

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