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Oxygen-17 NMR Study of the Uranyl Ion. II.[1] Correlation between ^{17}O NMR Chemical Shifts and Wavelengths of UV-Visible Absorption Bands of Uranyl Complexes

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^{17}O NMR chemical shifts, UV-visible and IR spectra of a series of $[UO_2L_n](ClO_4)_2$ (L=unidentate oxygen-donor ligand; n=coordination number) complexes in nonaqueous solvents have been measured. The electronic transition bands of the UO_2^{2+} entity shift toward lower energies with the increase in base strength of ligands in the equatorial plane. The asymmetric stretching frequencies of U=O bands are also affected by the base strength of equatorial ligands and correlated with the lowest electronic transition energies of uranyl complexes with the same geometry. The ^{17}O chemical shifts are shown to be related to the lowest electronic transition energies of uranyl complexes. It appears that oxygen isotope shifts in ^{17}O NMR spectra of the uranyl ion are predominantly attributed to the increase in the lowest electronic transition energies.

The electronic structure of dioxouranium(VI) (uranyl) ions has been extensively studied by UV-visible, infrared, and Raman spectroscopy.[2] In particular, much attention has been paid to ligation effects on the vibrational spectrum of the uranyl ion. Recently Bray and Kramer[3] showed that there are some correlations between spectroscopic parameters and ligand(L) basicity for UO_2(hexafluoroacetylacetonato)$_2$L. They reported that the asymmetric stretching frequencies of U=O bonds decrease with increasing the base strength of ligands L in the vapor phase and benzene solution.

Our interest in ligation effects on U=O bonds has led to the study of UV-visible, infrared, and ^{17}O NMR spectra of $[UO_2L_n](ClO_4)_2$,[4] in which the base strength of ligand L in the equatorial plane may be characterized by its donor number.[5] Electronic spectra of uranyl complexes exhibit a remarkable similarity, which implies that UV-visible absorption bands arise from electronic transitions within the UO_2^{2+} entity. The absorption bands could be divided into three groups with origins at 22050, 24150, and 27000 cm^{-1} representing the three components of the triplet state which is split by the equatorial field.[2a] Furthermore, the vibronic fine structure is superimposed on these absorption bands. We investigated the variation in the position of electronic transition bands by changing ligand L. It is also of interest to see whether the position of the bands is correlated with the uranyl asymmetric stretching frequency.

From the study of ^{17}O NMR spectroscopy of oxygen-containing compounds, it is evident that ^{17}O NMR chemical shifts are very sensitive to a change in the nature of oxygen bonding.[6] In this connection it is interesting to study ligation effects on the ^{17}O NMR spectrum of oxygen in the uranyl ion (uranyl oxygens hereafter). There are a few ^{17}O NMR studies of uranyl complexes,[7] but no systematic study has been carried out. In this paper ^{17}O chemical shifts of uranyl oxygens of some uranyl complexes are reported and interpreted in terms of the lowest electronic transition energies in UV-visible spectra. Oxygen isotope shifts in ^{17}O NMR spectra of enriched uranyl oxygens in aqueous solution[1] may also be interpreted in terms of the lowest electronic transition energies.

Experimental

Preparation of Uranyl Complexes. Methods in the literature[8] were used to prepare all the uranyl complexes used in this study. Hydrated uranyl perchlorate was refluxed with triethyl orthoformate at 50—60 °C for 1 h, followed by the addition of dried nonaqueous solvent L at room temperature. The resulting crystals of $[UO_2L_n](ClO_4)_2$ were filtered, washed with diethyl ether and dried under reduced pressure. In the case of DEF a yellow oil was formed at the bottom of the flask. The supernatant fraction was decanted and the residual oil was stirred with successive portions of diethyl ether. The resulting oil was dried under reduced pressure. Synthesized complexes, which are listed in Table 1, were identified by elemental analyses and/or ^{1}H NMR measurements.

NMR Measurements. ^{17}O NMR measurements of uranyl oxygens in natural abundance were carried out at 13.46 MHz on a JEOL JNM-FX 100 FT-NMR spectrometer. A spectral width of 20 kHz, 8 K data points, and a 90° pulse width of 10 μs were used. One hundred and fifty thousand transients were usually collected. All measurements were made at 20 °C and all chemical shifts were downfield relative to $H_2{}^{17}O$ in natural abundance. No bulk susceptibility correction was made.

Sample solutions for NMR measurements were prepared by dissolving uranyl complexes in nonaqueous solvent-(L)-CD_2Cl_2 (CD_3CN for LNO complex) mixture, where $5[UO_2L_n(ClO_4)_2]<$[free ligand]. An additional measurement was carried out in the case of TMU complex, where [free TMU]=0. The concentration of complexes was about 0.1 M (1 M=1 mol dm^{-3}), and less soluble complexes were studied in saturated solutions. Sample solutions were introduced into NMR microcells (Wilmad). The microcell was inserted in a 10 mm o.d. NMR tube (Wilmad) containing reference water.

^{17}O NMR measurements of uranyl oxygens enriched by using $H_2{}^{17}O$ (Merck, ^{17}O, 42.1; ^{18}O, 31.7 atom%) were carried out at 54.10 MHz on a JEOL JNM-GX 400 FT-NMR spectrometer. Detailed procedure for preparation of enriched uranyl oxygens is described in a previous paper.[1] The temperature of the solution was maintained at 24.4±0.1 °C.

UV-Visible and IR Spectra Measurements. UV-visible spectra (350—550 nm) were measured on a Shimadzu UV-365 spectrophotometer using 1 cm quartz cells. IR spectra in the region 4000—400 cm^{-1} were taken on a Hitachi 270-30 IR spectrophotometer using KRS-5 cells (Horiba). Sample solutions for UV-visible and IR measurements were prepared by dissolving each uranyl complex in the solvent corresponding to the equatorial ligand. An additional measurement was carried out for the TMU complex, where [free TMU]=0. The concentrations of sample solutions for UV-visible and IR spectra measurements were usually 0.01 and 0.3 M, respectively, and less soluble complexes were measured by using saturated solutions.

Results and Discussion

UV-Visible and IR Spectra. The electronic spectra of most uranyl complexes in this study exhibited three band groups with a well-defined vibronic structure, which are characteristic of uranyl complexes. On the other hand, no vibronic structure was observed in the third band group with the origin at 27000 cm^{-1} for TMU, LNO, and HMPT complexes. This arises from the fact that the third band group is overshadowed by an intense ligand-to-uranyl charge-transfer band when the base strength of equatorial ligands is considerably high. Assignment of the electronic states involved in the electronic absorption spectrum of the uranyl ion is still a matter of controversy, but the interpretation by McGlynn and Smith[2a)] is generally accepted. They suggested that the absorption band between 20500 and 30000 cm^{-1} results from excitation of an electron from the highest filled π-orbital to a nonbonding orbital on uranium (ϕ_u or δ_u).

It was found that an increase in base strength of equatorial ligands results in a bathochromic shift of the electronic transition bands. As shown in Fig. 1, $0' \leftarrow 0''$ band in the first electronic transition (band number I_0 after De Jaegere and Görller-Walrand's notation[9)]) shifts toward lower energies with the increase in base strength of equatorial ligands. The same trend was observed for $2' \leftarrow 0''$ band in the second transition (band number II_2[9)]) except for the HMPT complex. Belford *et al.*[10)] reported the similar results, in which absorption bands in visible region shifted toward higher energies with successive fluorination of acetylacetone in the bis(acetylacetonato)dioxouranium(VI), *i.e.* with decreasing the base strength of ligands.

These ligation effects on UV-visible spectra can be explained by McGlynn and Smith's suggestion.[2a)] According to the suggestion, the electron density of the ϕ_u or δ_u atomic orbitals of uranium might be enhanced by σ(L-M) electron donation of equatorial ligands. This may result in stabilization of energy levels of nonbonding orbitals, thus lowering the electronic transition energies. The enhanced electron density on the uranium also causes a loosening of the U=O bond because of increased electrostatic repulsion with the highly negative axial uranyl oxygens.[2b)] This is reflected in the asymmetric stretching frequency ν_{as} of the U=O bonds. It was observed, therefore, that the uranyl asymmetric stretching frequency is lowered by increasing base strength of equatorial ligands. These ligation effects on both UV-visible and infrared spectra give a good correlation between ν_{as} and the energy of $0' \leftarrow 0''$ band in the first electronic transition (ΔE_{I_0}), as shown in Fig. 2. The fact that the results for four-coordinated HMPT and TMU complexes deviated from the correlation line in Fig. 2 may be explained in terms of the difference in geometry between four-coordinated complexes (D_{4h}) and the other complexes (D_{5h}), by considering that absorption spectra of uranyl complexes can be affected by difference in the number and geometric disposition of equatorial ligands.[2f)] However, this explanation requires further study.

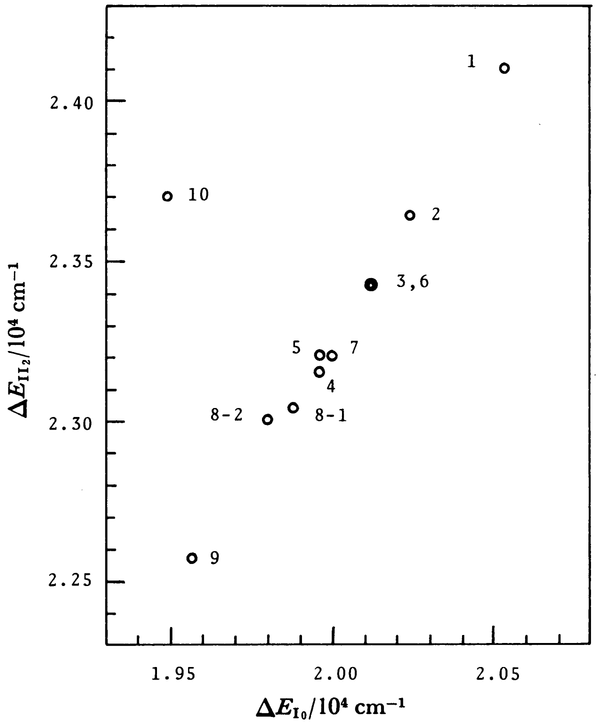

Fig. 1. Correlation of energies (ΔE_{II_2}) of $2' \leftarrow 0''$ bands in the second electronic transition with energies (ΔE_{I_0}) of $0' \leftarrow 0''$ bands in the first electronic transition. The figures correspond to those in Table 1.

In addition to the electronic interaction as mentioned above, the uranyl asymmetric stretching frequency is also affected by vibrational interaction, which is attributed to the coupling between the U=O stretching and the bending of bonds between uranium and equatorial ligands. Jones[11)] estimated

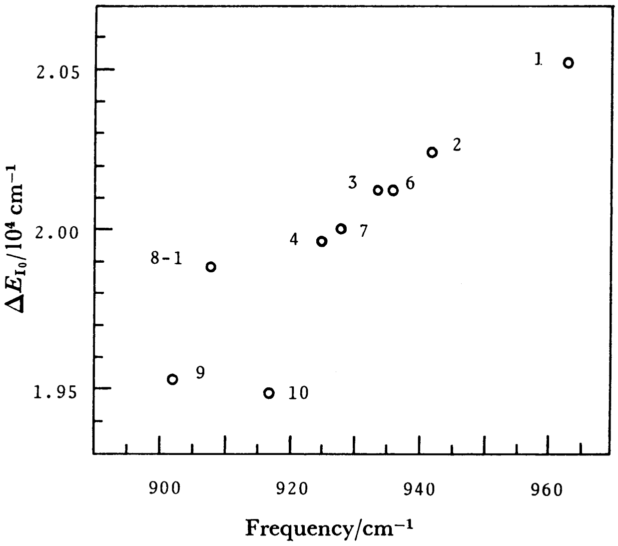

Fig. 2. Correlation of energies (ΔE_{I_0}) of 0′←0″ bands in the first electronic transition with the asymmetric stretching frequencies of the U=O bonds. The figures correspond to those in Table 1.

that the maximum alteration would be 3%. Furthermore, the effect of intermolecular interaction on ν_{as} can not be neglected when ν_{as} is measured in liquid sample. In the case of hydrated uranyl perchlorate, for example, ν_{as} measured in D_2O solution at pH 2.5 is about 10 cm^{-1} lower than that in H_2O solution at pH 2.5, while no variation in UV-visible spectra was observed in both the solutions. This phenomenon is ascribed to the solvent effect, where hydrogen bonds between uranyl oxygens and D_2O are stronger than those between uranyl oxygens and H_2O. It is known that the hydrogen bond contributes to weakening the U=O bond strength.[12] However, the solvent effect in aprotic solvents employed in this study is considered to be negligible.

From our results of ligation effects on both UV-visible and infrared spectra, we propose that ΔE_{I_0} in UV-visible spectra and ν_{as} in infrared spectra can be used as parameters of the complexing ability (or base strength) of equatorial ligands toward the uranyl ion. The parameters may be compared to the donor number,[5] which is defined as the enthalpy of complex formation between the given solvent and antimony pentachloride in 1,2-dichloroethane solutions. Figures 1 and 2 show that the base strengths of DEA and DEF toward the uranyl ion are almost equal to those of DMA and DMF, respectively, although there are considerable differences in the donor numbers each other. Fukutomi *et al.*[13] showed that the donor property of ligands is correlated with the E_B parameter[14] in equilibrium study on the anation reaction of uranyl complexes.

^{17}O NMR Chemical Shifts. ^{17}O chemical shifts ($\delta^{17}O$) measured in this study are summarized in Table 1. It is noted that ^{17}O resonances of uranyl oxygens shift downfield with increasing the base strength of equatorial ligands of the uranyl ion. This ligation effect on ^{17}O chemical shifts can be explained in terms of the electronic transition energy.

TABLE 1. SPECTROSCOPIC PARAMETERS FOR $[UO_2L_n](ClO_4)_2$ COMPLEXES IN SOLUTION

L[a]	C.N.[b]	λ_{I_0}[d] nm	λ_{II_2}[d] nm	$\nu_{as}(U=O)$[e] cm^{-1}	$\delta(^{17}O)$[h] ppm
1. H_2O	5	487	415	963	1119.0[f]
2. TMP	5	494	423	942	1122.5
3. DMF	5	497	427	934	1131.5
4. DMA	5	501	432	925	1133.3
5. DMSO	5	501	431	g)	1129.7
6. DEF	5	497	427	936	1131.2
7. DEA	5	500	431	928	1133.7
8-1. TMU	4[c]	503	434	908	1138.8
8-2. TMU	5	505	435	g)	1138.4
9. LNO	5	512	443	902	1137.7
10. HMPT	4	513	422	917	1138.8

a) Ref. 4. b) Coordination number in the equatorial plane of uranyl ion in solution, where $5[UO_2L_n(ClO_4)_2] < $[free ligand]. See Ref. 8. c) C.N., where [free TMU]=0. d) Precision of measurement: ±1 nm. Band numbers I_0 and II_2 refer to 0′←0″ band in the first electronic transition and 2′←0″ band in the second electronic transition, respectively. e) Precision of measurement: ±1 cm^{-1}. f) At pH 2.5. g) Unmeasurable due to masking by the absorption of ligand. h) Precision of measurement: ±0.5 ppm.

The nuclear shielding of ^{17}O nuclei can be approximated as the sum of diamagnetic (σ_d) and paramagnetic (σ_p) terms, $\sigma=\sigma_d+\sigma_p$.[15] It has been shown[16] that the paramagnetic term is principally responsible for the total shielding constant in ^{17}O nuclear shieldings. This paramagnetic term can be expressed as follows[17]:

$$\sigma_p^A = -\frac{2e^2\hbar^2}{3m^2c^2\Delta E}\langle r^{-3}\rangle_{2p}\sum_B Q_{AB},$$

where A is the nucleus under investigation, B represents all the other nuclei in the molecule, m is the electron mass, $\langle r^{-3}\rangle_{2p}$ is the average value of the reciprocal cube of the 2p orbital radius, and ΔE is the "mean" excitation energy of the molecule. $\sum Q_{AB}$ is related to the electronic charges and bond orders. To a first approximation, the ΔE can be equated to the excitation energy of the lowest excited state. Figgis *et al.*[18] established a linear relationship between the ^{17}O chemical shifts for oxyanions of the transition metals and the reciprocal of their lowest electronic transition energies. Kazanskii[19] also showed the correlation between the ^{17}O chemical shifts of both the terminal and bridge oxygen atoms in polyoxometalates and the wavelength of the first charge transfer. The data for the uranyl ion in aque-

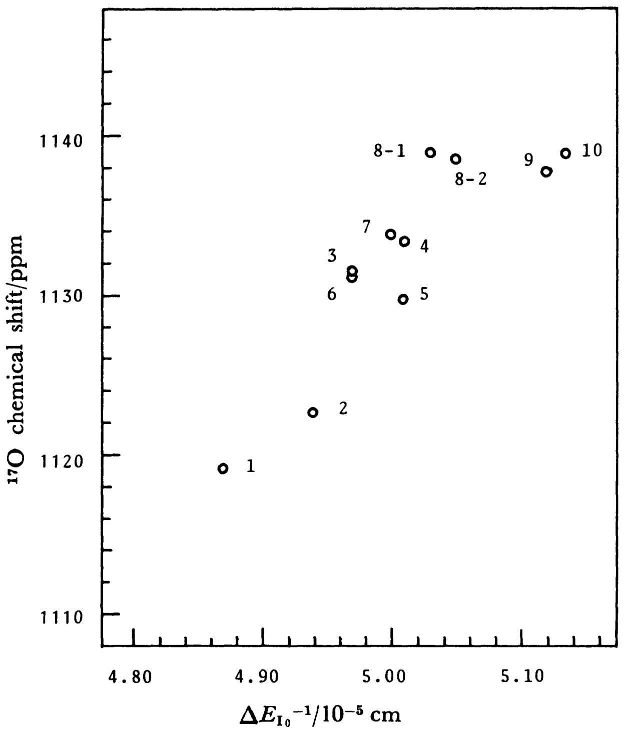

Fig. 3. Correlation of ^{17}O chemical shifts with the reciprocal of the lowest electronic transition energies. The figures correspond to those in Table 1.

ous solution (at pH 2.5, δ=1119.0 ppm; λ_{I_0}=487 nm) fall on the correlation line obtained by Figgis *et al.* This indicates that ΔE is the dominant factor in determining ^{17}O nuclear shielding of uranyl oxygens in uranyl complexes.

As shown in Fig. 3, a good correlation is observed between the ^{17}O chemical shifts and the reciprocal of the lowest electronic transition energies ($1/\Delta E_{I_0}$) of uranyl complexes. Besides the lowest electronic transition energy, the other factors such as U=O distance and the other electronic transition must be considered as minor factors. As mentioned above, the uranyl asymmetric stretching frequency, which can be a measure of the U=O bond distance,[20] changes with equatorial ligands. The variation in bond distance can affect ^{17}O nuclear shielding. Since an increase in U=O bond distance is expected to lead to an increase in ^{17}O nuclear shielding,[21] the ^{17}O chemical shift for the LNO complex may be lower than that expected from its lowest electronic transition energy (see Fig. 3). On the other hand, ΔE_{II_2} value for the HMPT complex is significantly higher than that expected from ΔE_{I_0} value, as shown in Fig. 1. Therefore, the contribution from the second electronic transition in the HMPT complex will be considerably smaller than in the other complexes, resulting in a low ^{17}O chemical shift.

Oxygen Isotope Shifts in ^{17}O NMR Spectra. In the previous paper[1] we assigned three peaks of ^{17}O-enriched uranyl oxygens to the signals of three isotopomers, *i.e.*, $[^{16}O{=}U{=}^{17}O]^{2+}$, $[^{17}O{=}U{=}^{17}O]^{2+}$, and $[^{18}O{=}U{=}^{17}O]^{2+}$. In order to support our previous results further, we measured the ^{17}O NMR spectrum of enriched uranyl oxygens at 54.10 MHz. As shown in Fig. 4, three peaks were much better resolved than those at 13.46 MHz. Chemical shifts for the signals of $[^{17}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ isotopomers were observed to be -0.059 ± 0.004 and -0.117 ± 0.004 ppm, respectively, relative to $[^{16}O{=}U{=}^{17}O]^{2+}$, which are more accurate than values reported previously.[1] A few data on the isotope shift through two bonds have been reported,[22] but no data are available for the isotope shift through two bonds in ^{17}O NMR except for the oxygen isotope shifts in the uranyl ion. It may be, therefore, of interest to interpret these isotope shifts.

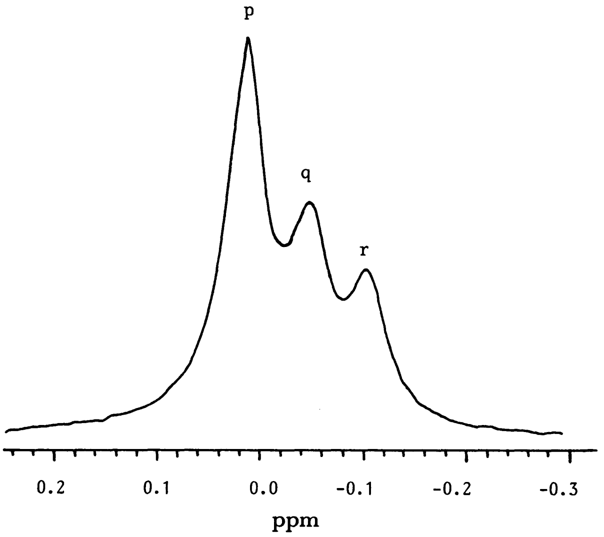

Fig. 4. ^{17}O NMR spectrum of the uranyl oxygens measured at 54.10 MHz. The uranyl oxygens were enriched by using $H_2{}^{17}O$ (42.1 atom%). $[UO_2{}^{2+}]$= 0.098 m and $[H^+]$=0.23 m (1 m=1 mol kg^{-1}). Typical ^{17}O spectral parameters are as follows: spectral width=1000 Hz, data points=16 K, scans=200, pulse width=10 μs. Peaks p, q, and r correspond to $[^{16}O{=}U{=}^{17}O]^{2+}$, $[^{17}O{=}U{=}^{17}O]^{2+}$, and $[^{18}O{=}U{=}^{17}O]^{2+}$, respectively.

Heavy substitution of the molecule commonly leads to the reduction of the zero point vibrational energies.[23] Since this reduction is larger in the ground state than in the electronically excited state, the electronic transition energies of substituted molecules are generally shifted toward higher energies. In view of this fact the lowest electronic transition ($0'\leftarrow0''$ band in the first electronic transition) of heavier isotopomers of the uranyl ion is expected to occur at higher energies. The increase in the lowest electronic transition energy, which is a dominant factor in determining the ^{17}O nuclear shielding of uranyl oxygens, will result in an increase in ^{17}O nuclear shielding. It is estimated from the correlation in Fig. 3 that the difference in chemical shifts between $[^{16}O{=}U{=}^{17}O]^{2+}$ and $[^{18}O{=}U{=}^{17}O]^{2+}$ at 24.4 °C corresponds to the difference of *ca.* 6.6 cm^{-1} in the lowest electronic transition energies. Unfortunately no experimental results are found for oxygen isotope shifts in the electronic absorption spectrum of the uranyl ion in aqueous solution. This small difference may be compared to the experimental value in $[UO_2Cl_4]^{2-}$, where the difference in the lowest electronic transition energies between $[^{16}O=U=^{16}O]^{2+}$ and $[^{18}O=U=^{18}O]^{2+}$ was observed to be 10 cm^{-1} at 4.2 K.[24]

Heavy substitution also leads to the change in U=O bond distance, but the contribution of this change to the ^{17}O nuclear shielding will be less important than that of the change in the lowest electronic transition energies, as indicated above. Mamayev *et al.*[25] demonstrated that, in a semi-empirical calculation of the isotope shifts in ^{13}C, ^{14}N, and ^{17}O NMR, the variation in the "mean" excitation energy cannot be left out of account on isotopic substitution of the molecule. It is considered that oxygen isotope shifts in ^{17}O NMR spectra of enriched uranyl oxygens can be explained only in terms of the change in the lowest electronic transition energies by isotopic substitution.

^{235}U–^{17}O Spin-Spin Coupling. Taking account of the fact that ^{17}O resonance of uranyl oxygens is very sharp, we intended to observe $^{235}U(I=7/2)$-^{17}O spin-spin coupling of enriched $^{235}UO_2^{2+}$ (*ca.* 90% ^{253}U) ion in aqueous solution. No fine structure was observed even at 65 °C. It appears that this is associated with a very small magnetic moment of ^{235}U nucleus. Oxygen isotope shifts measured at 65 °C for $^{235}UO_2^{2+}$ solution were somewhat lower than for $^{238}UO_2^{2+}$ solution at room temperature.

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References

1) Part I: W.-S. Jung, Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **57**, 2317 (1984).

2) a) S. P. McGlynn and J. K. Smith, *J. Mol. Spectrosc.*, **6**, 164 (1964); b) S. P. McGlynn, J. K. Smith, and W. C. Neely, *J. Chem. Phys.*, **35**, 105 (1961); c) J. I. Bullock, *J. Chem. Soc. (A)*, **1969**, 781; d) J. P. Day and L. M. Venanzi, *J. Chem. Soc. (A)*, **1966**, 1363; e) J. M. Haigh and D. A. Thornton, *J. Mol. Struct.*, **8**, 351 (1971); f) C. Görller-Walrand and S. De Jaegere, *Spectrochim. Acta*, **28A**, 257 (1972).

3) R. G. Bray and G. M. Kramer, *Inorg. Chem.*, **22**, 1843 (1983).

4) Ligand abbreviations: TMP=trimethyl phosphate; DMF=*N,N*-dimethylformamide; DEF=*N,N*-diethylformamide; DMA=*N,N*-dimethylacetamide; DEA=*N,N*-diethylacetamide; DMSO=dimethyl sulfoxide; TMU=1,1,3,3-tetramethylurea; LNO=2,6-lutidine *N*-oxide; HMPT=hexamethylphosphoric triamide.

5) V. Gutmann, "Coordination Chemistry in Non-Aqueous Solutions," Springer-Verlag, Berlin (1968).

6) W. G. Klemperer, *Angew. Chem., Int. Ed. Engl.*, **17**, 246 (1978).

7) S. W. Rabideau, *J. Phys. Chem.*, **71**, 2747 (1967); L. G. Mashirov, D. V. Suglobov, and V. A. Shcherbakov. *Radiokhimiya*, **17**, 881 (1975).

8) A. M. Hounslow, S. F. Lincoln, P. A. Marshall, and E. H. Williams, *Aust. J. Chem.*, **34**, 2543 (1981) and references cited therein.

9) S. De Jaegere and C. Görller-Walrand, *Spectrochim. Acta*, **25A**, 559 (1969).

10) R. N. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **14**, 169 (1960).

11) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958).

12) G. V. Sidorenko, R. B. Dushin, E. K. Legin, and D. N. Suglobov, *Radiokhimiya*, **23**, 407 (1981).

13) H. Doine, Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **57**, 1021 (1984).

14) R. S. Drago and R. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965); R. S. Drago, *Coord. Chem. Rev.*, **33**, 251 (1980).

15) N. F. Ramsey, *Phys. Rev.*, **78**, 699 (1950).

16) K. A. Ebraheem and G. A. Webb, *J. Magn. Reson.*, **25**, 399 (1977).

17) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1954).

18) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Proc. R. Soc. London, Ser. A.*, **269**, 469 (1962).

19) L. P. Kazanskii, *Koord. Khim.*, **3**, 327 (1977).

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

21) K. F. Miller and R. A. D. Wentworth, *Inorg. Chem.*, **18**, 984 (1979); R. G. Kidd, *Can. J. Chem.*, **45**, 605 (1967).

22) G. V. D. Tiers, *J. Chem. Phys.*, **29**, 963 (1958); R. A. Bell, C. L. Chan, and B. G. Sayer, *J. Chem. Soc., Chem. Commun.*, **1972**, 67; R. A. Bernheim and B. J. Lavery, *J. Chem. Phys.*, **42**, 1464 (1965).

23) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, D. Van. Nostrand, Princeton (1966).

24) R. G. Denning, T. R. Snellgrove, and D. R. Woodwark, *Mol. Phys.*, **32**, 419 (1976).

25) V. M. Mamayev, N. M. Sergeev, and K. A. Orazberdiev, *J. Struct. Chem.*, **18**, 38 (p. 31 English ed.) (1977); V. M. Mamayev and N. M. Sergeyev, *Chem. Phys. Lett.*, **34**, 317 (1975).