

Influence of the Base Strength of Ligand on Infrared Spectra of Uranyl(VI) Complexes in Solution

Woo-Sik Jung, Hiroshi Tomiyasu, and Hiroshi Fukutomi

Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-Ku, Tokyo 152, Japan

Jung-Sung Kim†

Department of Chemistry, Taegu University, Taegu 634, Korea (Received January 22, 1985)

Infrared spectra of a series of $[\text{UO}_2\text{L}_n](\text{ClO}_4)_2$ (L = unidentate oxygen-donor ligand; n = coordination number) complexes have been measured. A study of infrared spectra of uranyl ions in aqueous solution shows the possibility of intermolecular hydrogen bonding between uranyl oxygen atoms and H_2O . The uranyl asymmetric stretching frequencies are affected by the base strength of equatorial ligands, and the force constant of $\text{U}=\text{O}$ bonds are correlated with Gutmann's donor number. The variation in these force constants is interpreted in terms of the perturbation of electronic structures of uranyl moiety arising from ligation.

The nature of the uranyl ion (UO_2^{2+}) is unique in its structure and in its coordination chemistry. Oxyocations such as VO_2^+ and MoO_2^{2+} , in which V(V) and Mo(VI) have the formal valence configuration d^0 , have cis geometry, whereas $\text{UO}_2^{2+}(\text{f}^0)$ has always trans geometry. Coordination occurs in the plane perpendicular to the $\text{O}-\text{U}-\text{O}$ axis and the coordination number in the equatorial plane can be up to six. Most of uranyl complexes carry oxygen-donor ligand, and uranyl ions are considered to be a typical "hard" Lewis acid according to Pearson's definition.

We studied a ligation effect on $\text{U}=\text{O}$ bond by infrared spectroscopy and interpreted the results in terms of the perturbation of electronic structures of uranyl moiety by ligation in the equatorial plane.

The IR spectrum of uranyl perchlorate in H_2O is shown in Figure 1. The peak at 963 cm^{-1} corresponds to the uranyl asym-

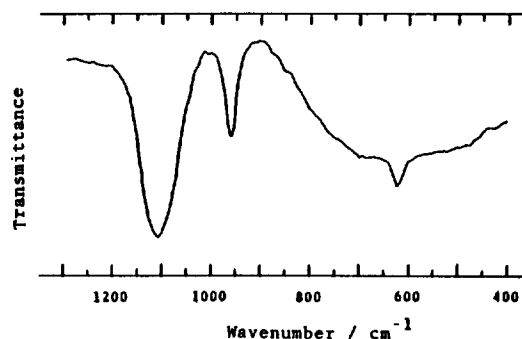


Figure 1. Infrared spectrum of uranyl perchlorate in H_2O .

metric stretching frequency and two peaks at 1110 and 626 cm^{-1} are assigned to ν_3 and ν_4 of perchlorate ions (T_d), respectively,⁷ which suggests that the perchlorate ion is not coordinated to the uranyl ion in solution as in the solid state⁸. The asymmetric stretching frequency in D_2O is about 10 cm^{-1} lower than that in H_2O . This fact indicates that the bond strength of $\text{U}=\text{O}$ bonds in D_2O is weaker than that in H_2O . This phenomenon may arise from intermolecular hydrogen bonding between uranyl oxygen atoms and bulk water rather than from intramolecular one between uranyl oxygen atoms and coordinated water because the rate of water exchange between the coordinated and bulk water is very fast ($k_{ex} = 9.8 \times 10^8\text{ sec}^{-1}$ at 25°C)⁹. It is noted that the uranyl oxygen atoms are reported to retain some negative charge.¹⁰ The intermolecular interaction, however, is considered to be negligible in aprotic solvents employed in this study compared with the interaction in water.

The uranyl asymmetric stretching frequencies ν_3 depend on the conditions under which the IR measurement was made, in particular on aggregate states of the complexes (solid, solution, gas). As shown in the Table 1, ν_3 is lowered by increasing the base strength of equatorial ligands. The observed decrease in ν_3 , which has also been observed for other complexes with in-

TABLE 1: Uranyl Asymmetric Stretching Frequencies and Force Constants of $\text{U}=\text{O}$ Bonds for $[\text{UO}_2\text{L}_n](\text{ClO}_4)_2$ Complexes

L ^a	C.N. ^b	D.N. ^c	ν_3^d cm^{-1}	f_1^e $\text{mdyne } \text{Å}^{-1}$
1. H_2O	5	18.0	963	7.71
2. TMP	5	23.0	942	7.37
3. DMF	5	26.6	934	7.25
4. DMA	5	27.8	925	7.11
5. DEF	5	30.9	936	7.28
6. DEA	5	32.2	928	7.16
7. TMU	4	29.6	908	6.85
8. HMPT	4	38.8	917	6.99

^aRef. 5 ^bCoordination number n in the equatorial plane of uranyl ion in solution. See Ref. 6 and 8b ^cRef. 12 ^dPrecision of measurement is $\pm 1\text{ cm}^{-1}$ ^eCalculated from eq 2 assuming that f_{12} is negligible.

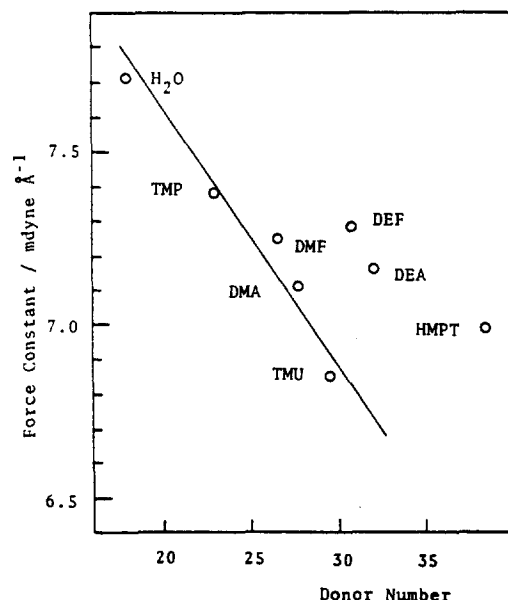


Figure 2. Correlation of force constants of U=O bonds with Gutmann's donor numbers.

creasing the ligand base strength,^{2,3} is attributed primarily to σ (ligand-metal) electron donation into an empty ϕ_u or d_u atomic orbital of the uranium atom. The enhanced electron density on the uranium atom destabilizes the U=O bonds by electrostatic repulsion with the highly negative axial oxygen atoms, thereby decreasing the vibrational frequency.

When valence force are assumed,¹¹ Eqs. 1 and 2 related the stretching and interaction force constants of the linear symmetric triatomic molecule, UO_2^{2+} , to vibrational frequencies ν_1 and ν_3 :

$$4\pi^2c^2\nu_1^2 = (f_1 + f_{12})/m_0 \quad (1)$$

$$4\pi^2c^2\nu_3^2 = (1 + 2m_0/m_u)(f_1 - f_{12})/m_0 \quad (2)$$

where m_0 and m_u are masses of ^{16}O and ^{238}U atoms, respectively, f_1 is the stretching force constant of the U=O bonds, f_{12} is the force constant for interaction of one U=O bond with the other U=O bond, and other symbols have the usual significance. From ν_3 and ν_1 (881 cm^{-1})^{3a} of the uranyl ion in aqueous solution, f_1 and f_{12} were calculated to be 7.52 and -0.20 mdyne \AA^{-1} , respectively.

As shown in Figure 2, the calculated f_1 value is well correlated with the donor number of equatorial ligand,¹² which is defined as the enthalpy of complex formation between the given solvent and antimony pentachloride in 1,2-dichloro-ethane solution. Figure 2 shows that the base strengths of DEA and DEF toward the uranyl ion are almost equal to those of DMA and DMF, respectively, whereas there are considerable differences in the donor number each other. Results of other reports^{14,15} demonstrated that donicities of DEA and DEF are almost the same as those of DMA and DMF, respectively.

The fact that force constant for the HMPT complex is much higher than that expected from the donor number of HMPT may be due to vibrational interactions¹⁶ which are not easily

estimated. These interactions arise from the fact that the asymmetric stretching involves movement of the uranium atom and the vibration is coupled to the bending vibrations of the bonds to the equatorial ligands. The extent of the coupling is expected to be dependent on the bending force constants of metal-ligand bonds and on masses of the ligands. It is noted that the HMPT is the bulkiest of ligands in this study.

The observed tendency for the ν_3 frequency to decrease as the increase in the base strength of equatorial ligands is explained electronically, as discussed above. In the case of the HMPT complex, both factors seem to be important. On the basis of the results in this study we will investigate ligation effects on U=O bonds by means of ^{17}O NMR spectroscopy.

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- (5) Abbreviations: TMP = trimethyl phosphate; DMF = N,N-dimethylformamide; DEF = N,N-diethylformamide; DMA = N,N-dimethylacetamide; DEA = N,N-diethylacetamide; TMU = 1,1,3,3-tetramethylurea; HMPT = hexamethylphosphoric triamide.
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