Raman spectrum of uranyl oxalate, malonate, salicylate, terephthalate and humate have been measured. The O=U=O symmetric stretching frequency of uranyl oxalate, malonate, terephthalate and humate had similar values, suggesting the same number of ligands co-ordinating to central uranium, i.e. one carboxyl group is co-ordinating to one uranium atom. The smaller frequency was observed in uranyl salicylate, suggesting the co-ordination of both carboxyl and phenyl groups, under the formation of a 6-membered chelate ring. *Ab initio* MO calculation supported this idea.

Short title: A Raman Spectroscopic Study of Organouranyl Compounds

1 Introduction

Complex formation of uranyl ions with the organic compounds is quite important for the safety assessment of uranium contaminated environment because it could result in significant increase in the concentration of dissolved uranium released into the geosphere. Various organic acids including oxalic[1], salicylic[2] and phthalic[2] acids have been considered as models for understanding the complexation of the uranyl to the organic acids including humic acid. This paper reports on the interaction of uranyl ions with the organic acids that have -COOH and -OH groups from its Raman spectrum measurements. Oxalic, malonic, salicylic, terephthalic and humic acids were selected as samples.

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*Department of Quantum Engineering and Systems Science, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo, Tokyo 113-8656, Japan, E-mail:tsu@qs.t.u-tokyo.ac.jp*
We have focused on the shift of O=U=O symmetric stretching frequency (Raman active, IR inactive) by the binding of ligand to the uranyl. The extent of the shift reflects the strength of complexation, i.e. the nature and the number of functional groups co-ordinated to the uranyl. The goal of this study is the speciation of the complexes formed by the interaction between organic compounds and uranyl ions.

2 Experimental

10ml of organouranyl solution was prepared by the equimolar mixture of uranyl solution and organic acids. The solution had been kept shaking for 24 hours at 25ºC prior to the measurements under the aerobic condition. The pH of the solution was adjusted so that the final pH should be around 4 to 5. All chemicals used in this study were of analytical grade and were supplied by Wako Pure Chemical Industries Ltd..

514.5nm emission line of an Ar⁺ laser was used as an emission source of Raman measurements. High resolution triple monochrometer was produced by the combination of a double monochrometer (Ritsu, MC-20LW, 1200L/mm) and a single monochrometer (Ritsu, MC-50N, 1800L/mm). CCD detector (JASCO, LN-CCD1100PB) was used as a detector of Raman signals. The detector was refrigerated with liquid nitrogen to reduce the thermal noise.

3 MO Calculation

"ab initio" MO(Molecular Orbital) calculation was carried out using quantum chemical calculation code Mulliken 2.0 (IBM Corp.) on IBM workstation 43P-133 using 6-31G basis set. Effective-Core Potential (ECP) Method was used to achieve reliable results for molecules containing uranium. In this approach, inner-shell electrons are eliminated from the calculation and their effects on valence electrons are replaced with ECPs parametrized to fit
observed atomic properties. This has dual advantage of including the most important contribution of relativistic effects to uranium chemistry and reducing computation cost as the basis set need only describe the valence orbitals.

Structure optimisation steps through values of selected nuclear co-ordinates and optimises the energy with respect to the remaining co-ordinates. Estimated precision of structure calculation is 0.003Å.

4 Results and Discussions

The O=U=O symmetric stretching vibration of dissolved UO$_2^{2+}$ ion is Raman active but infrared(IR) inactive, and observed at 870 cm$^{-1}$[3]. Upon co-ordination of ligand onto uranyl, the frequency shifts to smaller wavenumber due to the weakening of U=O bonding. The amount of frequency shift depends on the type of ligand co-ordinated, and a linear correlation between the frequency of O=U=O symmetric stretching frequency vibration and the average number of ligands co-ordinated equatorially to the central uranium atom has been established for various ligands[3]. If we apply this rule to the Raman frequency observed for organouranyl complexes, useful information can be obtained.

Fig.1 shows Raman spectra of uranyl oxalate, malonate, salicylate, terephthalate and humate with the spectra of oxalic, malonic, salicylic and terephthalic acids in the wavenumber range of 550 ~ 1100 cm$^{-1}$. Raman spectrum of humic acid could not be obtained because of strong fluorescence. The O=U=O symmetric stretching frequencies observed in these organouranyl complexes are summarised in Table 1. From this table, it is observed that the frequency shift upon co-ordination of organic ligands is similar, but the value for salicylate is somewhat larger than those for oxalate, malonate, phthalate and for humate.

Since there is a linear correlation between the number of ligands co-ordinated to uranyl and the frequency shift [3], this result suggests the number of ligands co-ordinated to
uranyl are the same in all these organouranyl complexes, i.e. one carboxyl group is co-
ordinated to one uranium atom, forming 4-membered bidentate ring. Similarity of the
Raman frequency obtained for uranyl oxalate and malonate suggests a small interaction to the
U=O bonding from the equatorial ligands except the first two oxygens and the distal carbon.
The similarity of Raman frequency observed in uranyl terephthalate also supports this idea.

A larger shift observed in salicylate compared to others may be interpreted as co-
ordination of both carboxyl and phenyl groups, under the formation of a 6-membered chelate
ring. This idea agrees with MO calculation results in which U=O bonding lengths is rather
similar among uranyl oxalate, malonate, phthalate and bidentate salicylate but a little larger
in uranyl chelate salicylate. Table 1 shows the values of U=O bond lengths calculated by MO
geometry optimisation for some organouranyl complexes. Fig. 2 shows the result of structural
optimisation of uranyl oxalate for an 1:1 complex.

The Raman frequency shift observed in uranyl humate is larger than those observed in
oxalate, malonate and terephthalate but smaller than that in salicylate. Bidentate co-
ordination of uranyl to carboxyl group is likely and the larger shift of humate compared to
oxalate, malonate and terephthalate is due to a large molecule size of humic acid. Of course, a part of uranyl ions interact with phenyl groups but their contribution to the spectra may be
little.

U=O bond length can be calculated from symmetric stretching Raman frequency
experimental value ($\omega_1$) through the U=O stretching force constant. If one considers that in
the linear symmetric model one has

$$\omega_1^2 = k * (F_{U-O} + F_{O-O})/16$$

where $F_{U-O}$ is the uranyl stretching and $F_{O-O}$ the central force constant between the two
oxygen atoms which may be either attractive (negative value) or repulsive (positive value)[4].
Neglecting $F_{O-O}$ one obtains
\[ F_{\text{U-O}} = 9.425 \times 10^{-6} \omega_1^2 \]

if one takes \( k = (1302.9)^2 \) to have units in \( \text{cm}^{-1} \) and \( \text{mdyn/Å} \). Jones has obtained empirical relation of \( \text{U=O} \) bond length \( R_{\text{U-O}} (\text{Å}) \) and \( F_{\text{U-O}}[5] \).

\[ R_{\text{U-O}} = 1.08 F_{\text{U-O}}^{-1/3} + 1.17 \]

By this relation, \( \text{U=O} \) bond lengths in the uranyl species can easily be obtained as shown in Table 1. This result agree with Denecke’s conclusion that \( \text{U=O} \) bond lengths are the same to within experimental error for EXAFS measurements[2]. But the result also shows that Raman should provide a very sensitive measure of bond distance - thus a very appreciable change of 5 \( \text{cm}^{-1} \) in Raman frequency corresponds to a change of only 0.002 Å units in \( \text{U=O} \) bond lengths. A slight change in equatorial plane may be reflected in Raman frequency, but is not observable in direct measurement of \( \text{U=O} \) bond length.

Still, there is relatively a large difference between the \( \text{U=O} \) bond lengths calculated from Raman frequency and those calculated by \textit{ab initio} MO calculation. This is mainly due to the lack of simulation of solvent in the latter, which obviously leads to shorter \( \text{U=O} \) bond lengths. However, our present study has shown that MO calculation as well as Raman spectrum measurement provides useful information of structure of molecules. Further study is worthwhile for the speciation of not only organouranyl complexes but also of various organic and inorganic actinyl complexes.

5 Conclusions

We have measured Raman spectrum of uranyl oxalate, malonate, salicylate, terephthalate and humate. The similarity of \( \text{O=U=O} \) symmetric stretching frequency of oxalate, malonate, terephthalate and humate suggested that the number of ligands co-ordinated to central uranium is the same, i.e. one carboxyl group is co-ordinated to one uranium atom. The smaller frequency observed in uranyl salicylate may be due to the co-
ordination of both carboxyl and phenyl groups, under the formation of a 6-membered chelate ring. MO calculation supported this idea.

References

Table 1.  Raman band, stretching force constant, Raman frequency calculated bond length and MO calculated bond length of U=O bonding in various organouranyl complexes.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Raman Band (cm$^{-1}$)</th>
<th>Frequency Shift (cm$^{-1}$)</th>
<th>$F_{U=O}$ (md/Å)</th>
<th>$R_{U=O}$ (Raman) (Å)</th>
<th>$R_{U=O}$ (MO) (Å)</th>
</tr>
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<tbody>
<tr>
<td>none</td>
<td>870.3</td>
<td>0.0</td>
<td>7.139</td>
<td>1.731</td>
<td>1.645</td>
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<tr>
<td>oxalate</td>
<td>851.0</td>
<td>19.3</td>
<td>6.826</td>
<td>1.739</td>
<td>1.687</td>
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<tr>
<td>malonate</td>
<td>849.3</td>
<td>21.0</td>
<td>6.798</td>
<td>1.740</td>
<td>1.691</td>
</tr>
<tr>
<td>salicylate</td>
<td>844.7</td>
<td>25.6</td>
<td>6.725</td>
<td>1.742</td>
<td>1.708*(ch), 1.698**(bi)</td>
</tr>
<tr>
<td>terephthalate</td>
<td>849.5</td>
<td>20.8</td>
<td>6.802</td>
<td>1.740</td>
<td>----</td>
</tr>
<tr>
<td>humate</td>
<td>847.5</td>
<td>22.8</td>
<td>6.770</td>
<td>1.741</td>
<td>----</td>
</tr>
</tbody>
</table>

*value for 6-membered chelate salicylate (with phenyl)

**value for 4-membered bidentate salicylate (no phenyl)
Fig. 1. Raman spectra of uranyl oxalate, malonate, terephthalate, salicylate and humate.
Fig. 2  Geometry optimisation of uranyl oxalate by *ab initio* MO calculation for 1:1 model.