

Title	Raman spectroscopic study on $\text{NpO}_2^{2+}$ - $\text{Ca}^{2+}$ interaction in highly concentrated calcium chloride
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Citation	Journal of Radioanalytical and Nuclear Chemistry (2014), 301(1): 293-296
Issue Date	2014-07
URL	<a href="http://hdl.handle.net/2433/199861">http://hdl.handle.net/2433/199861</a>
Right	The final publication is available at Springer via <a href="http://dx.doi.org/10.1007/s10967-014-3130-1">http://dx.doi.org/10.1007/s10967-014-3130-1</a> .
Type	Journal Article
Textversion	author

1 Short Communication

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3 **Raman Spectroscopic Study on  $\text{NpO}_2^+$ - $\text{Ca}^{2+}$  Interaction in Highly Concentrated**  
4 **Calcium Chloride**

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14  
15 **Abstract**

16 Coordination circumstance of neptunyl ion in concentrated  $\text{CaCl}_2$  solutions was  
17 analyzed by Raman spectrometry. Besides the symmetric stretch ( $\nu_1$ ) mode of  $\text{NpO}_2^+$   
18 and  $\text{NpO}_2^{2+}$ , the asymmetric stretch ( $\nu_3$ ) mode of  $\text{NpO}_2^+$  was found. The Raman  
19 intensity of the  $\nu_3$  mode increased with the concentration of  $\text{CaCl}_2$  in the system. This  
20 would be attributable to the cation-cation interaction between  $\text{Np(V)}$  and  $\text{Ca(II)}$ .

21  
22 **Keywords**

23 Raman spectrometry, neptunium, neptunyl, calcium chloride, cation-cation interaction

25 **Introduction**

26 The mutual coordination of actinyl ions especially in oxidation state (V) [1] is known as  
27 "cation-cation interaction (CCI)". The first evidence of CCI has been found in a  
28 complexation of Np(V)-U(VI) [1]. Following it, the CCIs of Np(V) with various cations  
29 in aqueous solutions have been found [2-17]. Multiply charged cations [2-8] or  
30 oxo-cations [1,9-17] contact with Np(V) dissolved in aqueous solutions as neptunyl ion,  
31  $\text{NpO}_2^+$ .

32 Absorption spectrophotometry is the possible analytical method for finding the  
33 CCI of Np(V) complexes [1-10,13-15,17]. This technique is effective for the systems  
34 containing Np(V) and cations with valence (III) or higher. As divalent cations, only  
35 CCIs of Np(V)-Hg(II) and Np(V)-Pb(II) are reported, in which the CCI was not clearly  
36 distinguished in absorption spectra [2]. To our knowledge, the CCI between Np(V) and  
37 divalent alkaline earth cations has not been found yet.

38 Another analytical method, Raman spectrometry, is effective for finding the  
39 CCI of Np(V) complexes via stretching vibrations of  $\text{NpO}_2^+$  [9,12,13]. This method was  
40 applied for the pairs of actinyl cations, that is,  $\text{NpO}_2^+$ - $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$ - $\text{NpO}_2^+$ , and  
41  $\text{NpO}_2^+$ - $\text{NpO}_2^{2+}$ .

42 Calcium chloride hexahydrate,  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , possesses a low melting point,  
43 303 K. The melt is identical with  $6.9 \text{ mol dm}^{-3}$  (M) and  $9.6 \text{ mol kg}^{-1}$  (*m*)  $\text{CaCl}_2$  aqueous  
44 solution. Cations, anions, and water molecules in molten hydrate salts, so-called hydrate  
45 melts, contact each other continuously by forming a quasi-lattice structure [18]. The  
46 coordination circumstance of solute ions dissolved in the media is different from that in  
47 water abundant systems, and hence chemical behavior of actinides in concentrated  
48  $\text{CaCl}_2$  systems is of interest [19,20]. In the present study, we investigated the stretching  
49 vibrations of  $\text{NpO}_2^+$  in highly concentrated  $\text{CaCl}_2$  solutions by Raman spectrometry.

50 The possibility of the CCI between Np(V) and Ca(II) is discussed.

51

## 52 **Experimental**

53 Calcium chloride dihydrate,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , of analytical grade (Wako Pure Chemical  
54 Industries, Ltd.) was used without purification. Weighed amounts of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and  
55  $\text{H}_2\text{O}$  were mixed for preparing solutions with various concentrations of  $\text{CaCl}_2$ . In order  
56 to analyze Np(VI) and Np(V) in the same sample, a nitric acid solution containing  $^{237}\text{Np}$   
57 was used as a starting material. A portion of the solution was once dried by heating,  
58 where the dried salt is a nitrate of Np(VI) and Np(V), and then the  $\text{CaCl}_2$  solution  
59 prepared was added. The concentration of Np was 0.01 M. The sample volume prepared  
60 was 0.2 mL. The sample was taken in a quartz cell with 2 mm light path and the cell  
61 was sealed. Electronic absorption spectra of the samples were measured in the  
62 wavelength range from 340 to 1350 nm at 0.5 nm intervals by using an UV/Vis/NIR  
63 spectrophotometer (Shimadzu, UV-3100PC).

64 Raman spectra were measured by using a Raman spectrophotometer  
65 (NRS-3100, JASCO). A green laser with the wavelength of 531.9 nm was used at the  
66 output power of 57.6 mW. The measurement interval of a charge-coupled device (CCD)  
67 detector was set to be every  $0.3 \text{ cm}^{-1}$ . The operations of each 3-seconds measurement  
68 were accumulated by 300 times. The experimental temperature was 298 K.

69 It should be noted that the water activity in hydrate melts is extremely small  
70 [19], and the solubility of oxygen in the media is very low [21]. The redox reaction of  
71 solutes in the media is hence deeply suppressed [20]. The Raman spectra and absorption  
72 spectra of the sealed samples remained the same throughout the experiment. The molar  
73 ratio of Np(VI)/Np(V) in our system estimated by using molar absorptivities [22] was 3.

74

75 **Results and discussion**

76 The literature data of CCIs found for Np(V) are summarized in Table 1. It is clear that  
77 absorption spectrophotometry is a powerful tool for finding the CCI of Np(V). The  
78 absorption band of  $\text{NpO}_2^+$  at *ca.* 980 nm is sensitive to the CCI, which results in a  
79 shoulder peak at higher wavelength of the absorption band. Clear increase of  
80 absorbance of the shoulder peak has been found for the complexation of  $\text{NpO}_2^+$  with  
81  $\text{VO}_2^+$  [9],  $\text{UO}_2^{2+}$  [1,5,10,17], or  $\text{NpO}_2^{2+}$  [15]. For the CCIs between Np(V) and divalent  
82 cations ( $\text{Hg}^{2+}$  and  $\text{Pb}^{2+}$ ), the two distinct absorption bands were not observed [2]. In the  
83 present  $\text{CaCl}_2$  systems, no shoulder peak was found for the Np(V) absorption band, but  
84 a red shift from 985.2 nm to 987.6 nm was found with the increase of  $\text{CaCl}_2$   
85 concentration.

86 The Raman spectra obtained are shown in Fig. 1. Three Raman bands were  
87 found in the range of 680 to 900  $\text{cm}^{-1}$ . Since it was confirmed by absorption  
88 spectrophotometry that the samples contain both Np(V) and Np(VI), these Raman bands  
89 are assigned to vibrational modes of  $\text{NpO}_2^+$  and  $\text{NpO}_2^{2+}$  species. The Raman frequency  
90 of the symmetric stretch ( $\nu_1$ ) mode of hydrated  $\text{NpO}_2^+$  is reported to be 766-767  $\text{cm}^{-1}$   
91 [9,12,23,24], while that of hydrated  $\text{NpO}_2^{2+}$  854-863  $\text{cm}^{-1}$  [23-25]. In Fig. 1, the Raman  
92 bands at 766-768  $\text{cm}^{-1}$  and 835-839  $\text{cm}^{-1}$  obtained are assigned to be  $\nu_1$  modes of  
93 hydrated neptunyl chlorides of Np(V) and Np(VI), respectively.

94 The complexation of Np(V) with trivalent metal cations via the oxo moiety of  
95  $\text{NpO}_2^+$  has been reported in a pioneering work of CCI [2]. The Raman intensity of the  
96 band at 802-805  $\text{cm}^{-1}$  shown in Fig. 1 clearly increases with the concentration of  $\text{CaCl}_2$ .  
97 This suggests that  $\text{Ca}^{2+}$  contacts with O of  $\text{NpO}_2^+$ . It is of interest that, in Raman  
98 spectroscopic studies on CCI of Np(V)-V(IV) [9] and Np(V)-Np(V) [12,13], the  $\nu_3$   
99 band of  $\text{NpO}_2^+$  which is not Raman-active was observed. Similar phenomenon may

100 have occurred in the present study.

101 The symmetric stretch ( $\nu_1$ ) mode of linear YXY-( $D_{\infty h}$ ) type molecules is  
102 Raman-active while the asymmetric stretch ( $\nu_3$ ) mode of them is infrared-active (not  
103 Raman-active) [26]. The  $\nu_3$  mode turns to Raman-active for linear YXZ-( $C_{\infty v}$ ) type  
104 molecules [26].  $NpO_2^+$  possesses two Np=O bonds. If the covalency of two Np=O  
105 bonds and/or the apparent mass of two O atoms vary through the complexation of  
106  $NpO_2^+$  with  $Ca^{2+}$ ,  $NpO_2^+$  would act as a YXZ-( $C_{\infty v}$ ) type molecule. This means that the  
107  $\nu_3$  mode appears in the Raman spectrum. The  $\nu_3$  frequency of  $NpO_2^+$  found for the CCI  
108 of Np(V)-Np(V) is  $37\text{ cm}^{-1}$  larger than its  $\nu_1$  frequency [12]. In the present study, the  
109 Raman band at  $802\text{-}805\text{ cm}^{-1}$  is *ca.*  $37\text{ cm}^{-1}$  larger than the  $\nu_1$  band of  $NpO_2^+$  ( $766\text{-}768$   
110  $\text{cm}^{-1}$ ). The Np concentration of 0.01 M may be too small to found the CCIs of  
111 Np(V)-Np(V) [10-14] and/or Np(V)-Np(VI) [1,15,16]. The Raman band found at  
112  $802\text{-}805\text{ cm}^{-1}$  would hence be the  $\nu_3$  band of  $NpO_2^+$  and the increase of its Raman  
113 intensity would be attributable to the complexation of Np(V) with  $Ca^{2+}$  via the oxo  
114 moiety of  $NpO_2^+$ .

115

## 116 **Conclusions**

117 A Raman band corresponding to the  $\nu_3$  mode of  $NpO_2^+$  was found for the highly  
118 concentrated  $CaCl_2$  system. This would be attributable to the complexation of Np(V)  
119 with  $Ca^{2+}$  via the oxo moiety of  $NpO_2^+$ . Absorption spectrophotometry is not effective  
120 for studying the Np(V)-Ca(II) interaction, while Raman spectrometry is useful to find  
121 the CCI.

122

## 123 **Acknowledgment**

124 This research was partly supported by Grants-in-Aid for Scientific Research (No.

125 23760827) from the Ministry of Education, Culture, Sports, Science and Technology,

126 Japan.

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167

168 **Table 1** Cations for CCIs of Np(V) in aqueous solutions.

Valence	Cation	Medium	Analytical method <sup>a</sup>	Reference
(II)	Ca <sup>2+</sup>	Chloride	Raman spectrometry	This study
	Hg <sup>2+</sup>	Perchlorate	Absorption spectrophotometry	[2]
	Pb <sup>2+</sup>	Perchlorate	Absorption spectrophotometry	[2]
(III)	Al <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2]
	Sc <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2]
	Cr <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2,3]
	Fe <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2,4,5]
	Ga <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2]
	Rh <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[6]
			Infrared spectrometry	
	In <sup>3+</sup>	Perchlorate	Absorption spectrophotometry	[2,7]
	BiO <sup>+</sup>	Perchlorate	Absorption spectrophotometry	[2]
(IV)	VO <sup>2+</sup>	Perchlorate	Absorption spectrophotometry	[9]
			Raman spectrometry	
	Th <sup>4+</sup>	Perchlorate	Absorption spectrophotometry	[5,8]
		Perchlorate	LIPAS	[8]
(V)	NpO <sub>2</sub> <sup>+</sup>	Perchlorate	Absorption spectrophotometry	[10]
		Perchlorate	HEXS	[11]
		Perchlorate	Raman spectrometry	[12]
		Nitrate	Absorption spectrophotometry	[13,14]
		Nitrate	EXAFS	[14]
		Nitrate	Raman spectrometry	[13]
(VI)	UO <sub>2</sub> <sup>2+</sup>	Perchlorate	Absorption spectrophotometry	[1,5,10,15]
		Perchlorate	Potentiometric measurement	[1]
			Proton relaxation measurement	
		Perchlorate	LAXS	[16]
		Perchlorate	LIPAS	[8]
	NpO <sub>2</sub> <sup>2+</sup>	Perchlorate	Raman spectrometry	[12],
		Nitrate	Absorption spectrophotometry	[17]
			Microcalorimetry	
		Perchlorate	Absorption spectrophotometry	[1,15]
		Perchlorate	Potentiometric measurement	[1]
		Proton relaxation measurement		
	Perchlorate	LAXS	[16]	

169 <sup>a</sup> EXAFS: Extended X-ray Absorption Fine Structure, HEXS: High-Energy X-ray Scattering, LAXS:  
170 Large-Angle X-ray Scattering, LIPAS: Laser -Induced PhotoAcoustic Spectroscopy.

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175 **Figure Caption**

176 Fig. 1 Raman spectra of 0.01 M Np in concentrated CaCl<sub>2</sub> solutions. Background  
177 spectrum was subtracted. Raman intensity was normalized by sum of peak areas.

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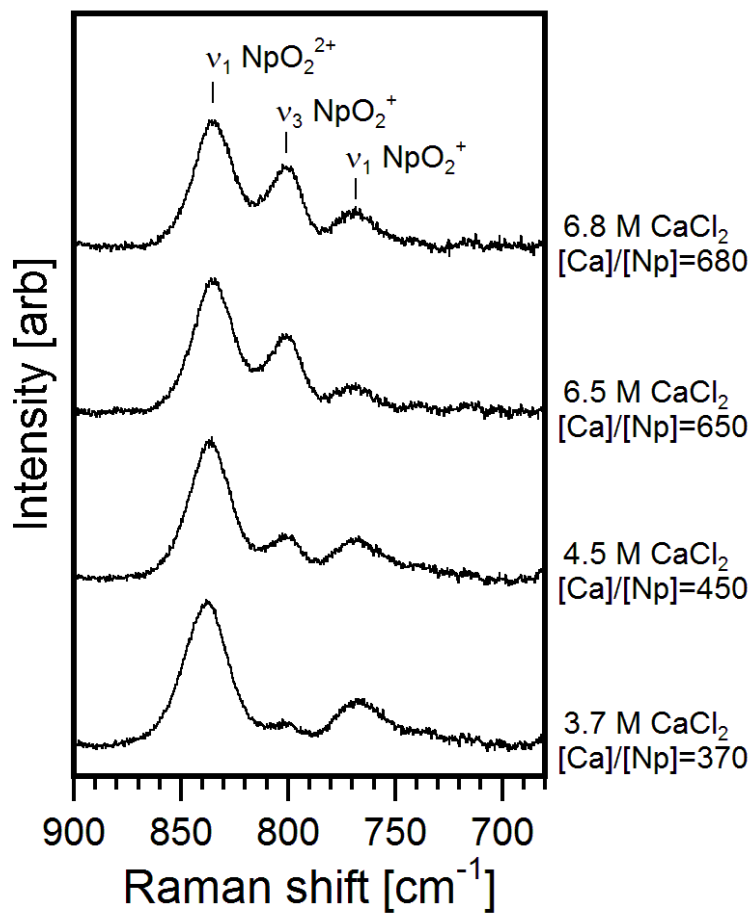
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Fig. 1 (T. Fujii et al.)