

RAMAN SPECTROSCOPIC STUDIES ON SPECIFIC INTERMOLECULAR INTERACTION OF URANYL β -DIKETONATO COMPLEX WITH $B(C_6F_5)_3$ UNDER SUPERCRITICAL CO_2

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INTRODUCTION

Supercritical CO_2 (sc- CO_2) has the potential to be used as an alternative green medium to traditional nonaqueous solvents for synthesis of medical compounds and fabrication of polymers of drug delivery system.^[1-6] Moreover, boron compounds have been studied as interest materials for synthesis of medical compounds and drug delivery system.^[1, 2, 7, 8]

In order to design effective reaction processes of medical compounds in sc- CO_2 , it is necessary to examine structures of boron compounds and metal complexes in sc- CO_2 and affinity between boron compounds and metal complexes in sc- CO_2 . Recently, it was reported that bonding between boron of $B(C_6F_5)_3$ (Tris(pentafluorophenyl)borane) and uranyl oxygen of uranyl complex is formed in non-aqueous solvent.^[9] Furthermore, we have examined intermolecular interactions between solute and sc- CO_2 by measuring Raman spectra of sc- CO_2 and $UO_2(dfh)_2DMSO$ (dfh = 1,1,1,2,2,6,6,7,7,7-decafluoroheptane-3,5-dionate, DMSO = dimethyl sulfoxide) in sc- CO_2 , and found that Lewis acid-Lewis base (LA-LB) interactions is formed between uranyl oxygen of $UO_2(dfh)_2DMSO$ and CO_2 carbon.^[10] However, little information has been available concerning the effects of added boron compounds on the structure of metal complexes and the interactions of boron compounds with metal complexes in sc- CO_2 .

In this present study, hence, we measured Raman spectral shift of U=O symmetric stretching (ν_1) of $UO_2(dfh)_2DMSO$ in sc- CO_2 containing $B(C_6F_5)_3$.

EXPERIMENTAL MATERIALS

The $UO_2(dfh)_2DMSO$ was synthesized by the same method as reported previously.^[11] 1,1,1,2,2,6,6,7,7,7-decafluoro-heptane-3,5-dione (Hdfh, Matrix Science, 97 %) was used without purification. Dimethyl sulfoxide (DMSO, Wako Pure Chemical, Ind. Ltd., 99 %) was stored over 4A molecular sieves. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, Wako Pure Chemical, Ind. Ltd., 95 %) was used without purification. CO_2 gas of 99.999% (TOMOE SHOKAI Co., Ltd.) was used in the present study.

APPARATUS AND PROCEDURE

The high-pressure cell body (volume = 819 cm³) with three sapphire windows (TAIATSU Glass Co., Ltd.) was made from stainless steel (SUS316). The optical path length of cell and the volume of sample are 2.6 cm and 8.1 cm³, respectively. Raman spectra of sc-CO₂ and solutes in sc-CO₂ were measured by a Raman spectrophotometer (JASCO RMP-200) equipped with a single monochromatic spectrograph system with a grating of 1800 lines/mm. The light source is a semiconductor laser (Nd:YVO₄) operating at 532 nm with a power of 100 mW. Raman spectral measurements under high pressure were performed by the same method as reported previously.^[12]

RESULTS AND DISCUSSION

RAMAN SPECTRA OF CO₂ IN sc-CO₂ AND sc-CO₂ CONTAINING B(C₆F₅)₃

The Raman spectra of pure gaseous CO₂ have been known to have two narrow bands at about 1388 (ν_u) and 1286 cm⁻¹ (ν_l), which are due to a Fermi resonance between the harmonic $2\nu_2$ of the bending mode and the ν_1 of symmetric stretching mode.^[13-15] We measured Raman spectra (ν_u and ν_l bands) of neat sc-CO₂ at 40 °C in the pressures range from 9.0 to 25.0 MPa (density; 0.47 < ρ (g·cm⁻³) < 0.88) to investigate the dependence of ν_u and ν_l bands on density of sc-CO₂. The results are shown in Figure 1. As seen from Figure 1, the ν_u and ν_l bands of sc-CO₂ shift linearly to lower wavenumbers with increasing density, *i.e.*, the red-shifts are about 1.0 cm⁻¹ and 2.0 cm⁻¹, respectively. These results are consistent with those reported previously.^[16, 17]

On the other hand, it has been reported that the red-shift from CO₂ bands of neat sc-CO₂ are caused by LA-LB interaction between UO₂(dfh)₂DMSO of uranyl oxygen and CO₂ carbon.^[10] Hence, we measured ν_u and ν_l bands of sc-CO₂ containing B(C₆F₅)₃ (5.0×10^{-2} M (M = mol·dm⁻³)) under the same conditions as neat sc-CO₂ system to examine whether the intermolecular interactions of sc-CO₂ with B(C₆F₅)₃ exist or not. As a result, it was found that the ν_u and ν_l bands of sc-CO₂ containing B(C₆F₅)₃ show similar red-shift to those of neat sc-CO₂ (Figure 1). These results indicate that the intermolecular interaction such as LA-LB interaction between CO₂ and B(C₆F₅)₃ does not exist in the present experimental conditions.

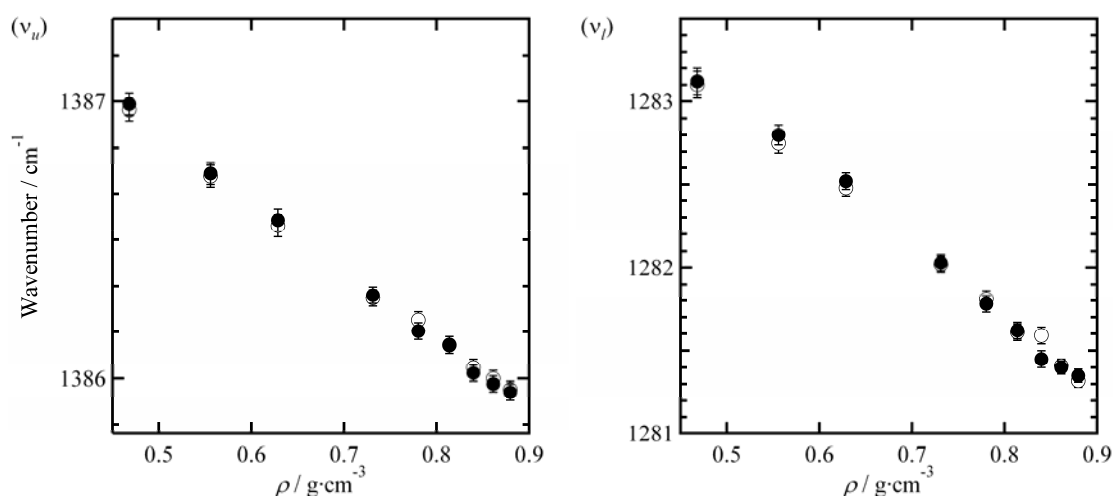


Figure 1. Plots of wavenumbers for ν_u and ν_l bands of neat sc-CO₂ (○) and sc-CO₂ containing B(C₆F₅)₃ vs. density. The concentrations of B(C₆F₅)₃ is 5.0×10^{-2} M (●)

RAMAN SPECTRA OF U=O SYMMETRIC STRETCHING OF $\text{UO}_2(\text{dfh})_2\text{DMSO}$ IN sc-CO_2 CONTAINING $\text{B}(\text{C}_6\text{F}_5)_3$

It has reported that bonding between boron of $\text{B}(\text{C}_6\text{F}_5)_3$ and uranyl oxygen of uranyl complex is formed in non-aqueous solvent, and that the LA-LB interaction between $\text{UO}_2(\text{dfh})_2\text{DMSO}$ of uranyl oxygen and CO_2 carbon in sc-CO_2 .^[9,10] From these previous reports and the Raman results explained above, it is expected that in sc-CO_2 containing $\text{UO}_2(\text{dfh})_2\text{DMSO}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ CO_2 competes with $\text{B}(\text{C}_6\text{F}_5)_3$ in the coordination to the uranyl oxygens of $\text{UO}_2(\text{dfh})_2\text{DMSO}$. Hence, we measured Raman spectral shift of U=O symmetric stretching (ν_1) of $\text{UO}_2(\text{dfh})_2\text{DMSO}$ (5.0×10^{-2} M) in sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ (1.0×10^{-2} - 5.0×10^{-2} M) under the pressure range (10.0 - 25.0 MPa at 40 °C: $0.63 < \rho < 0.88$), under which $\text{B}(\text{C}_6\text{F}_5)_3$ dissolves sufficiently in sc-CO_2 . It was found that the ν_1 bands shift to lower wavenumber with an increase in concentration of $\text{B}(\text{C}_6\text{F}_5)_3$ compared with those in sc-CO_2 containing only $\text{UO}_2(\text{dfh})_2\text{DMSO}$ (Figure 2), and that in sc-CO_2 system containing $\text{B}(\text{C}_6\text{F}_5)_3$ (5.0×10^{-2} M) the ν_1 bands show the constant wavenumber regardless of the variation in density of sc-CO_2 . These results reveal that the red-shift of ν_1 bands observed in sc-CO_2 containing $\text{UO}_2(\text{dfh})_2\text{DMSO}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ is due to that the LA-LB interaction between $\text{UO}_2(\text{dfh})_2\text{DMSO}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ is stronger than that between $\text{UO}_2(\text{dfh})_2\text{DMSO}$ and CO_2 , and that the interaction between $\text{UO}_2(\text{dfh})_2\text{DMSO}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ is existed even in the high density region of CO_2 .

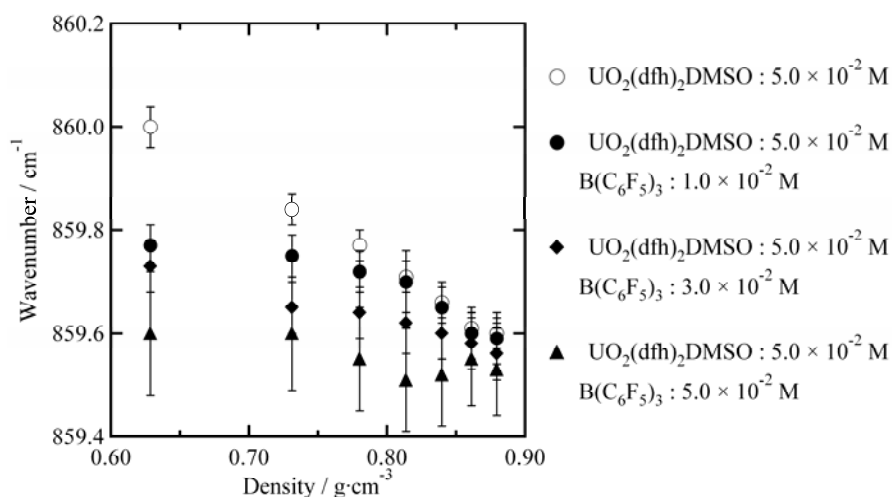


Figure 2. Plots of wavenumbers for ν_1 band of $\text{UO}_2(\text{dfh})_2\text{DMSO}$ in sc-CO_2 (\circ : 5.0×10^{-2} M) and that of $\text{UO}_2(\text{dfh})_2\text{DMSO}$ in sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ vs. density. The concentrations of $\text{B}(\text{C}_6\text{F}_5)_3$ are 1.0×10^{-2} (\bullet), 3.0×10^{-2} (\blacklozenge), and 5.0×10^{-2} M (\blacktriangle).

CONCLUSION

In the present study, we have observed the Raman bands (ν_u and ν_l) of sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ in the pressure range from 9.0 to 25.0 MPa at 40 °C and U=O symmetric stretching (ν_1) of $\text{UO}_2(\text{dfh})_2\text{DMSO}$ in sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ in the pressure range from 10.0 to 25.0 MPa at 40 °C. As a result, it was found that the ν_u and ν_l bands of CO_2 in sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ show similar red-shift to those of neat sc-CO_2 , and that the Raman spectra of ν_1 of $\text{UO}_2(\text{dfh})_2\text{DMSO}$ in sc-CO_2 containing $\text{B}(\text{C}_6\text{F}_5)_3$ shift to lower wavenumber with an increase in concentration of $\text{B}(\text{C}_6\text{F}_5)_3$ compared with those in sc-CO_2 containing only $\text{UO}_2(\text{dfh})_2\text{DMSO}$. In addition, the ν_1

bands in sc-CO₂ system containing B(C₆F₅)₃ (5.0×10^{-2} M) show the constant wavenumber regardless of the variation in density of sc-CO₂. From these results, it is proposed that the LA-LB interaction (U=O···B) between uranyl oxygen and boron of B(C₆F₅)₃ is formed in sc-CO₂. Furthermore, the LA-LB interaction between UO₂(dfh)₂DMSO and B(C₆F₅)₃ is stronger than that (U=O···C) between UO₂(dfh)₂DMSO and CO₂.

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