

Raman Spectroscopic Studies on Intermolecular Interactions of β -diketones and Their Complexes with CO₂ Molecules under Supercritical Conditions

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We have measured the vibrational motions of neat supercritical CO₂ (ScCO₂), and ScCO₂ containing β -diketones and their uranyl complexes using Raman spectroscopy to investigate intermolecular interactions of ScCO₂ with solutes. Two Raman peaks of CO₂ molecules corresponding to bending mode mainly ($\nu_u = 1388 \text{ cm}^{-1}$ for the gaseous CO₂) and symmetric stretching one mainly ($\nu_l = 1286 \text{ cm}^{-1}$) were measured in the pressure range of 8 to 25 MPa at 40 °C (density in $\text{g}\cdot\text{cm}^{-3}$: $0.28 < \rho < 0.88$) by high-pressure Raman spectrophotometer. In the neat ScCO₂ system, the peaks of ν_l and ν_u were found to show red-shift linearly by about 3 cm^{-1} and 1.5 cm^{-1} , respectively. In the ScCO₂ systems containing β -diketones, it was found that the ν_l and ν_u bands of ScCO₂ shift to lower wavenumber compared with those of neat ScCO₂ in the low density region, and approach to those of neat ScCO₂ with an increase in density. On the other hand, the ν_l and ν_u bands of ScCO₂ systems containing uranyl β -diketonate complexes show similar red-shift to those of neat ScCO₂. These results indicate that Lewis acid-Lewis base interactions and hydrogen bonding exist between carbonyl oxygen of β -diketones and carbon of CO₂, and between OH group of β -diketones and oxygen of CO₂ in ScCO₂ containing β -diketones respectively, and that such interactions are scarcely formed in the ScCO₂ containing uranyl β -diketonate complexes because of the absence of free C=O and OH groups.

Introduction

Supercritical carbon dioxide (ScCO₂) has numerous desirable features such as environmental acceptability, inexpensiveness, non-reactivity, and easy control of solvent properties with a slight variation of density.^[1] Hence, ScCO₂ is expected to be used as alternative green medium to organic solvents for chemical reaction, separation.^[2,3]

In order to apply ScCO₂ in various fields, it is necessary to design CO₂-philic molecules which have high solubility in ScCO₂. It is reported that the solubility of compounds into ScCO₂ is enhanced by fluorination, and that this is due to the specific interaction of ScCO₂ with fluorinated solutes or the high repulsion between fluorine atoms.^[4] Recently, hydrocarbons substituted with carbonyl group(s) such

as aldehydes, ketones, and acetates have been paid attention as economical and environmentally benign CO₂-philic compounds. It is proposed that the Lewis acid-Lewis base (LA-LB) interaction between carbon of ScCO₂ and oxygen of carbonyl group(s) play important role for the enhancement of solubility. In addition to LA-LB interaction, high solubility is considered to be attributed to hydrogen bonds between oxygen of ScCO₂ and hydroxyl group(s) (OH \cdots O) and/or hydrogen atoms attached to carbonyl carbons or α -carbon atoms (CH \cdots O).^[5] Studies on their interactions have been studied using IR spectroscopic analysis^[6], Raman spectroscopic analysis^[7], NMR measurement^[8], and theoretical analysis^[9]. In particular, Raman spectroscopy have been used for studying gaseous, liquid, solid^[10], and supercritical CO₂^[11]. However, little information has been available concerning effects of added solutes on the structure of ScCO₂ and the interactions of CO₂ with solutes in ScCO₂.

Hence, we measured Raman spectra of neat ScCO₂ and ScCO₂ containing β -diketones [acetylacetone (Hacac), trifluoroacetylacetone (Htfacac), hexafluoroacetylacetone (Hhfacac)] and their uranyl complexes [UO₂(β -diketonato)₂dmsO] (dmsO = dimethyl sulfoxide) by changing the pressure from 8 to 25 MPa at 40 °C (density in g \cdot cm⁻³: 0.28 < ρ < 0.88) to study the intermolecular interactions of ScCO₂ with solutes.

Experimental

Acetylacetone (Hacac) (Kanto Chemical Co., Inc.), trifluoroacetylacetone (Htfacac) and hexafluoroacetylacetone (Hhfacac) (Wako Pure Chemical Ind. Ltd.) were used without further purification. Dimethyl sulfoxide (Kanto) was stored over 4A molecular sieves prior to use. Pure grade CO₂ (purity of 99.999%, TOMOE SHOKAI Co., Ltd.) was used in the present study. The UO₂(β -diketonato)₂dmsO complexes were synthesized according to the procedure in the literature^[12], and recrystallized from dichloromethane.

The high-pressure cell body with 216 cm³ is made from hastelloy with three sapphire windows (TAIATSU Glass Co., Ltd.). The optical path length of cell and the volume of sample were 1.7 cm and 0.54 cm³, respectively. The temperature was controlled with electric heating rods put into cell body and detected by a thermocouple inserting inside the cell. The pressure was controlled with the syringe pump (ISCO Model-260D) connected to stainless steel tube with 1/16 inch. The pressure to the cell was given by exerting CO₂ gas via the syringe pump from the head of cell. The samples were stirred by directly injecting CO₂ gas to the cell. The Raman spectra of CO₂ molecules were measured after standing approximately 15 min for equilibrium between solutes and CO₂.

The Raman spectra of CO₂ molecules were measured by Raman spectrophotometer (JASCO RMP-200) equipped with single monochromater spectrograph, a grating of 1800 gr/mm, and the charge coupled device (CCD) detector. The source was an argon ion laser operating at a wavelength of 532 nm with a power of 100 mW.

Result and Discussion

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 symmetric stretch ν_1 .

We performed Raman spectra measurements of neat ScCO_2 at $40\text{ }^\circ\text{C}$ in the pressures range from 8 to 25 MPa to investigate the dependence of ν_l and ν_u bands on density. The results are shown in Figure 1. As seen from Figure 1, the peaks of ν_l and ν_u bands of ScCO_2 shift linearly to lower wavenumbers with increasing density, *i.e.*, the red-shifts are about 1.5 cm^{-1} and 3 cm^{-1} , respectively. These results are consistent with those reported previously.^[11]

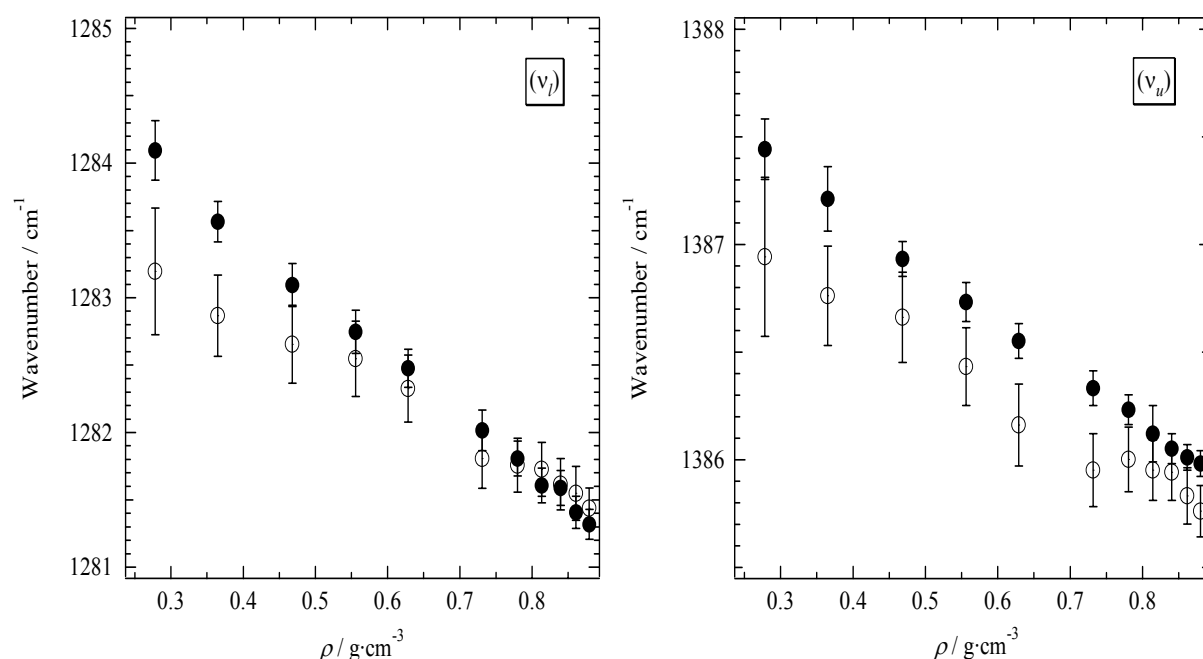


Figure 1. Plots of wavenumbers for ν_l and ν_u bands of neat ScCO_2 (●) and ScCO_2 containing Hacac (○) vs. density.

Similarly, we measured the Raman spectra of ScCO_2 containing Hacac, Htfacac, Hhfacac of $1.3 \times 10^{-1}\text{ M}$ to examine effects of added solutes on the structures and vibrational motions of ScCO_2 . Figure 1 displays the plots of wavenumbers for the ν_l and ν_u bands of ScCO_2 containing β -diketones against the densities. Both bands are found to shift to lower wavenumbers as well as in neat ScCO_2 , that is, the red-shifts are about 2 cm^{-1} and 1 cm^{-1} , respectively. Furthermore, it is observed that the ν_l and ν_u bands of ScCO_2 containing β -diketones are shifted to lower wavenumbers compared with those of neat ScCO_2 in the low density region, and approach to those of neat ScCO_2 with an increase in density. These differences of red-shift between neat ScCO_2 and ScCO_2 containing β -diketones suggest the existence of solute-solvent interactions such as LA-LB interactions and $\text{OH}\cdots\text{O}$ and/or $\text{CH}\cdots\text{O}$ proposed by Wallen *et al.*^[5-b, 7-b] The $\text{C}=\text{O}$ bond length of CO_2 molecules should become long with increasing the affinities of β -diketones for CO_2 accompanied by the LA-LB interactions between the carbonyl oxygen atoms as electron donor and the carbon atom of CO_2 molecules as electron acceptor. The $\text{C}=\text{O}$ bonds of CO_2 molecules are also affected by the $\text{OH}\cdots\text{O}$ hydrogen

bonding between enolic protons on β -diketones and the oxygen atoms of CO_2 . These solute-solvent interactions are considered to lead to the results that the ν_l and ν_u bands of ScCO_2 containing β -diketones shift to lower wavenumbers compared with those of neat ScCO_2 . The larger shifts in the low density region are due to the fact that the ratio of solute to solvent in the low density region is relatively larger than those in the high density region.

On the basis of this interpretation, it is expected that the density dependence of ν_l and ν_u bands in the ScCO_2 containing uranyl β -diketonato complexes shows similar tendency to that in the neat ScCO_2 system, because the interactions between ScCO_2 and uranyl β -diketonate complexes should be small due to the absence of free carbonyl and OH groups. Hence, we measured the ν_l and ν_u bands of ScCO_2 containing uranyl β -diketonate complexes under the same conditions as those of the ScCO_2 systems containing β -diketones. The results are shown in Figure 2.

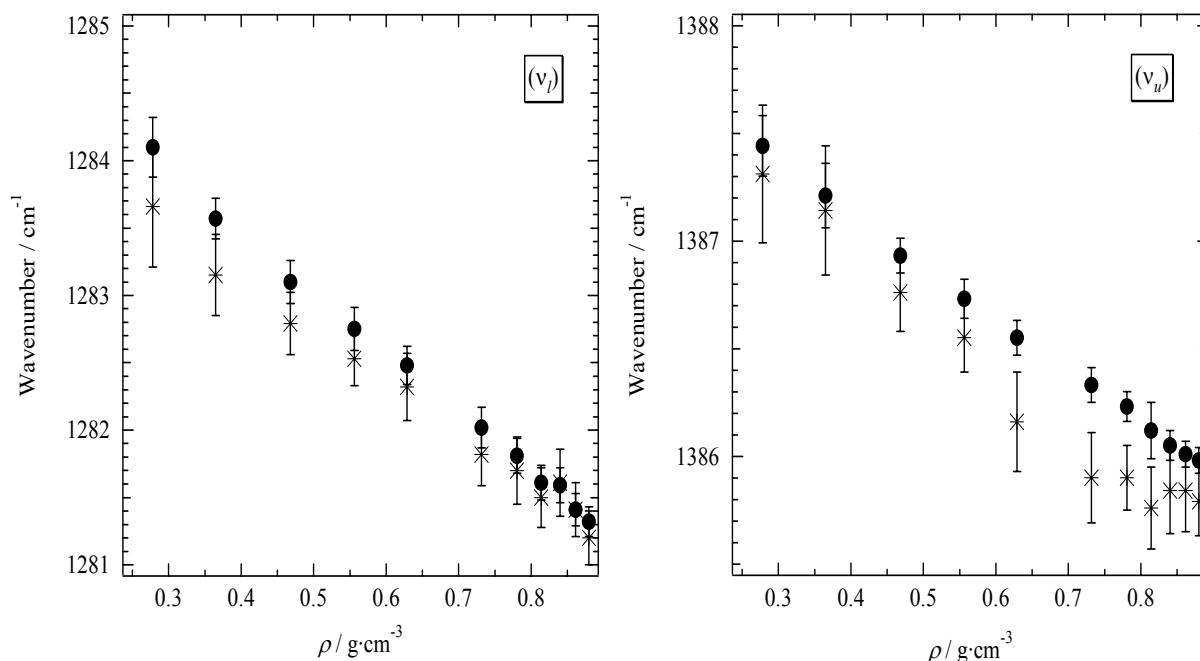


Figure 2. Plots of wavenumbers for ν_l and ν_u bands of neat ScCO_2 (●) and ScCO_2 containing $\text{UO}_2(\text{Hhfacac})_2\text{dms0}$ (*) vs. density.

As expected, the plots of wavenumbers for ν_u and ν_l of ScCO_2 containing uranyl β -diketonate complexes are analogous to those of neat ScCO_2 . Especially, in the low density region ($\rho < 0.6$), the shift to lower wavelength compared to neat ScCO_2 shown in Figure 1 is not observed in Figure 2.

Consequently, it is supported that the LA-LB interactions and $\text{OH}\cdots\text{O}$ hydrogen bonding exist between β -diketones and ScCO_2 .

Conclusion

The Raman spectral differences between neat ScCO_2 and ScCO_2 containing β -diketones indicate that the structures of CO_2 molecules in ScCO_2 change with increasing density, and support that the

LA-LB interaction($C=O\cdots C$) and $CH\cdots O$ and/or $OH\cdots O$ hydrogen bonding exist in the $ScCO_2$ system containing β -diketones. Furthermore, the phenomenon that the whole structures and vibrational motions of $ScCO_2$ are influenced by the interactions between CO_2 molecules and solutes existing in small amounts is very interesting. This observation is due to Raman spectral measurements of CO_2 molecules in $ScCO_2$ containing solutes.

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