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Articles

Concentration and Solvent Effects upon Carbonyl Streching Frequency Shifts of Raman Spectra; 4-Substituted Benzaldehydes

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From Raman spectra, the νC=O frequencies of 4-substituted benzaldehydes were found to correlate with the σ_p values of the 4-x atom or group as well as the acceptor number (AN) values of solvents. In various solvents, the νC=O frequency of benzaldehyde decreased upon the increase of benzaldehyde concentration. This shift was mainly due to the hydrogen bonding between the carbonyl oxygen and/or aldehydic proton of benzaldehyde and the solvent molecules. Over the 1-80 volume % change, the νC=O frequency of benzaldehyde down shifted from 1709.4 cm^{-1} to 1700.2 cm^{-1} in CCl$_4$ solution and from 1703.0 cm^{-1} to 1698.0 cm^{-1} in C$_2$H$_5$OH solution. This is due to the fact that hydrogen bonding between the benzaldehyde and C$_2$H$_5$OH was much stronger than that between the benzaldehyde and the other solvents.

Introduction

Spectral differences observed by recording vibrational spectra of compounds in various solvents are important to understand interactions between solutes and solvents. The IR study of solute/solvent interaction for a variety of chemical compounds containing C=O, C≡N functional groups with fixed concentration (1%) has been reported by Nyquist group.[1~5] They have shown that the carbonyl stretching mode, νC=O, for 4-x-benzaldehydes increases in frequency as the value for Hammett σ_p increase.[6,7] Previously we have studied the solvent effect on group frequencies of CN and CO stretching modes.[8,9]

In this work, a Raman spectroscopic study has been performed on 4-x-benzaldehyde in various solvents in order to further understand solute/solvent interactions. The concentration dependence and substituent effect of νC=O frequency were thoroughly investigated. This work will become basis for the establishment of Raman spectra-structure relationship in the future in conjunction with the identification of new compounds.

Experimental

Raman spectroscopic apparatus used in this study is Spex model 1403 equipped with 0.85m Double monochromator and RCA C31034 PM tube detector. A 50 mW laser beam of 514.5 nm wavelength from an argon ion laser (Coherent Innova 90-5) was used and the Raman scattering radiation from the grating was collected at 90° to the incident beam. Raman spectra were recorded using IBM compatible 386 PC along with SPEX DM 3000R softwares.

All of the spectra shown were obtained by single scan at a rate of 0.2 cm^{-1}/0.3 sec with slit settings of 400/400/400/400 μm. Reagent grade chemicals (Aldrich Chemical Co.) were used without further purification. Samples were sealed in glass capillary tubes of i.d. 0.8 mm. The solvents used are listed in the tables.

Results and Discussion

The Raman data of νC=O frequencies for 4-x-benzaldehydes in various solvents are given in Table 1 where X=F, Cl, Br, H, C$_6$H$_5$, H$_3$CO, (CH$_3$)$_2$N. All of the Raman active modes of 4-x-benzaldehydes are IR active modes because the point group of these molecules belong to C_s. Figure 1 shows the Raman spectrum of pure benzaldehyde. Several 4-x-benzaldehydes in various solvents exhibit two Raman bands in the region expected for the νC=O mode, and the two bands are attributed to Fermi resonance interaction between the νC=O and an overtone of out-of-plane aldehydic CH bending mode. Higher frequency side of the Raman band was assigned to νC=O as in the Nyquist's IR study.[6] The carbonyl stretching frequencies of 4-x-benzaldehydes decreased as solvent polarity increased. The νC=O mode for each of the 4-x-benzaldehydes occurs at the highest frequency in CCl$_4$ solution. In CCl$_4$ solution, the νC=O frequencies of 10% 4-x-benzaldehydes occurs in the region 1683.0-1710.6 cm^{-1}, and in CH$_3$OH solution occurs in the region 1657.4-1710.4 cm^{-1}. The difference in νC=O frequencies for various solutes amounted to 27.6 cm^{-1} in CCl$_4$ solution, while difference was 53.0 cm^{-1} in CH$_3$OH. These tendencies are in good agreement with the results of Nyquist's IR study.[6] The νC=O frequencies for 4-x-benzaldehydes are affected by intermolecular hydrogen bonding between the solvent proton and the lone pair electrons of carbonyl oxygen.

In order to study the solute/solute interaction for the νC=O frequency we examined νC=O Raman shift as the volume % of benzaldehyde increased in each solvent. In Nyquist's IR study, concentration of all the solutes were fixed to 1%. Generally, in concentrated solution (more than 10%), the IR bands become very broad while the Raman bands remains very sharp. The Raman data for the νC=O frequency of benzaldehyde in various volume % are given in Table

Table 1. Comparison of carbonyl streching frequencies (cm^{-1}) for 10% 4-x-benzaldehydes in various solvents

X Solvents	F (0.06)	Cl (0.23)	Br (0.23)	H (0.00)	C$_6$H$_5$ (−0.18)	H$_3$CO (−0.27)	(CH$_3$)$_2$N (−0.83)	AN
Carbon tetrachloride	1702.6	1705.5	1710.6	1706.0	1703.0	1699.4	1683.0	8.6
Carbon disulfide	1702.2	1706.1	1708.8	1705.4	1701.4	1698.2	1682.0	
Benzene	1701.6	1705.1	1709.0	1703.5	1701.2	1698.4	1677.8	8.2
Acetonitrile	1698.4	1703.1	1709.2	1702.9	1699.6	1696.0	1673.6	18.9
Benzonitrile	1698.2	1703.3	1708.2	1701.7	1698.6	1696.2	1672.4	15.5
Chloroform	1697.0	1700.9	1709.2	1702.1	1698.2	1695.6	1662.2	23.1
Ethyl alcohol	1698.0	1704.3	1710.8	1701.4	1700.8	1698.4	1658.2	37.1
Methyl alcohol	1696.0	1702.5	1710.4	1702.1	1700.4	1698.6	1657.4	41.3
Isopropyl alcohol	1699.2	1705.2	1710.6	1702.2	1702.6	1698.2	1661.4	33.5

*( ) represents Hammett σ_p values

Table 2. Raman data for the carbonyl streching frequencies (cm^{-1}) for benzaldehyde in various solvents

Solvent volume%	CCl$_4$	CS$_2$	C$_6$H$_6$	CH$_3$CN	C$_6$H$_6$CN	CHCl$_3$	C$_2$H$_5$OH	CH$_3$OH	(CH$_3$)$_2$CHOH
1	1709.4	1705.8	1704.9	1703.3	1702.3	1702.3	1703.0	1703.9	1703.4
10	1706.0	1705.4	1703.5	1702.9	1701.7	1702.1	1701.4	1702.1	1702.2
20	1704.8	1703.4	1702.9	1702.1	1701.3	1701.5	1700.6	1701.5	1701.8
40	1702.4	1702.0	1701.9	1700.9	1701.1	1701.3	1699.4	1700.7	1701.2
60	1701.4	1702.4	1701.1	1700.3	1700.7	1700.7	1698.8	1700.1	1700.8
80	1700.2	1700.2	1700.1	1699.9	1700.1	1700.5	1698.0	1699.9	1700.4
Pure	vC=O : 1695.0 cm^{-1}								
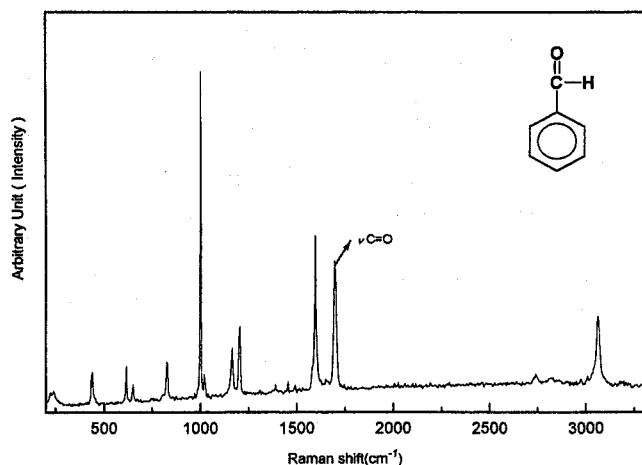
Figure 1. Raman spectrum of benzaldehyde.
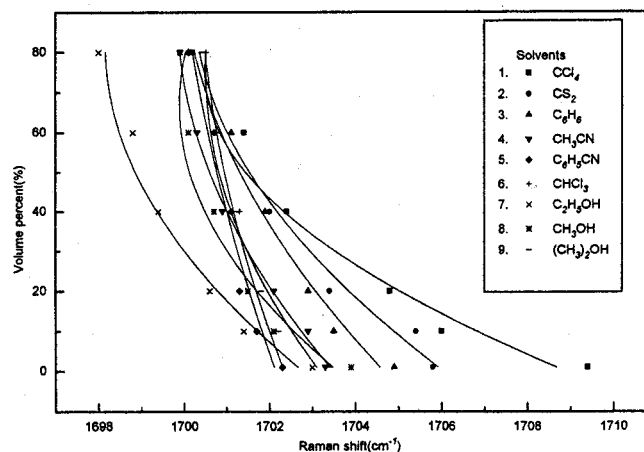
Figure 2. A plot of vC=O of benzaldehyde in various solvents *vs* volume percent of benzaldehyde.

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When the concentration of benzaldehyde in each solvent increased the vC=O streching mode shifted to lower frequency by solute-solute hydrogen bond. Figure 2 shows plots of the data in Table 2. The vC=O frequency of pure benzaldehyde was observed at 1695 cm^{-1}. As shown in Figure 2, vC=O frequency of benzaldehyde was shifted from 1709.4 cm^{-1} (1%) to 1700.2 cm^{-1} (80%) in CCl$_4$ solution by 9.2 cm^{-1}. While in C$_2$H$_5$OH, the vC=O frequency of benzaldehyde in the same volume % range was shifted to low frequency from 1703.0 cm^{-1} to 1698.0 cm^{-1} by 5.0 cm^{-1}. In these concentra-

tion ranges the magnitude of hydrogen bond strength change between carbonyl oxygen and aldehyde proton of benzaldehydes in CCl$_4$ was about two times (9.2/5.0) larger than that in C$_2$H$_5$OH. These red shift results suggest that the hydrogen bond strength changes in nonpolar solvents are larger than in polar solvents, as the benzaldehyde concentration increase from 1% to 80%. There is an exception for the C$_2$H$_5$OH which shifts to red much larger than the other polar solvents. With this experimental data only, it is difficult to explain the above exception quantitatively. Since the factors which
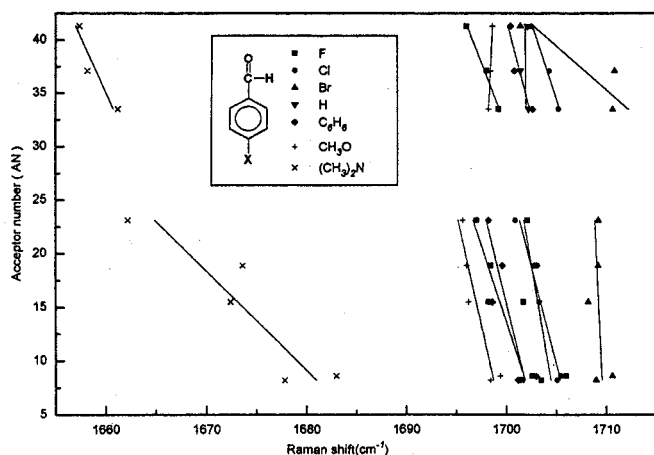
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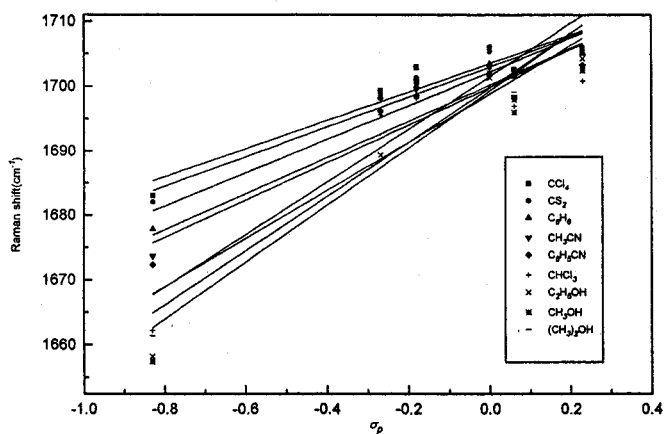**Figure 3.** A plot of νC=O for m 10% 4-x-benzaldehyde in various solvents *vs.* AN.

Figure 4. A plot of νC=O *vs.* Hammett σ_p for each of the 10% 4-x-benzaldehydes in various solvents.

affect the red shift of vibrational lines are not only by hydrogen bond but also by many other factors such as repulsive collisions (blue shift), dipole-dipole attractive interactions (red shift), and van der Waals interactions, etc.[10,11] In the low benzaldehyde concentration, the hydrogen bond interaction between benzaldehyde and polar solvent was much stronger than between the benzaldehyde and the other nonpolar solvents. In Figure 2, one would expect benzaldehyde-solvent hydrogen bond strength difference on abscissa, while benzaldehyde-benzaldehyde hydrogen bond strength difference on ordinate. It is known that phase dependent frequency shifts can be attributed to intermolecular interactions between identical molecules, while in dilute solution the observed frequency shifts reflect the solvent-solute interactions.[12]

The solvent acceptor number (AN) values of the solvents show a pseudo-correlation with the carbonyl stretching vibrations of 4-x-benzaldehydes, as in Nyquist's IR study. Figure 3 shows plots of the νC=O frequencies for each of the 4-x-benzaldehydes in the various solvents *vs.* AN of each solvent. In Figure 3 we note that the points corresponding to -(CH₃)₂N substituent [4-dimethylamino-benzaldehyde] were the most sensitive relationship with the change of solvent A.N. values.

Those alcohols in the condensed phase are intermoleculary hydrogen bonded between solutes and it is also possible for the intermolecular hydrogen bond between alcoholic OH group and the C=O group of the benzaldehyde. In this case, the intermolecular hydrogen bonding, R-OH : O=C would be the strongest one where the C=O group was the most basic group. As shown in Figure 3, the linear plot for 4-(dimethyl amino) benzaldehyde is distinctly different from the essentially linear plots exhibited by the other solvents used in this study. This result was due to the strongest intermolecular hydrogen bond formed between the proton of solvent and the C=O group of 4-(dimethyl amino) benzaldehyde.

The σ_p values are a measure of the inductive and resonance contribution of the para substituent to the carbonyl group. The negative σ_p values indicate the electron contribution to the carbonyl group, while positive σ_p values indicate the electron withdrawal from the carbonyl group.[13] Figure 4 shows plots of the νC=O frequency *vs.* σ_p for the 4-x group in 4-x-benzaldehydes in each solvent. The νC=O frequency for the 4-x-benzaldehydes increases as the electron contribution to the C=O group decreases. This tendency shows similar results with the Nyquist's 1% solution of IR study.[6] In Figure 4, we suggest that the solute/solvent interaction includes the interaction of the solvent with the C=O group of solutes as well as the 4-x-substituent, presumably with electron cloud distribution of the phenyl group for the 4-x-benzaldehydes.

Conclusions

The Raman νC=O frequencies for 4-x-benzaldehydes increase as the electron contribution to the C=O group decrease. The AN values of solvent and the σ_p values of the 4-x atom or group for 4-x-benzaldehydes appear to correlate with the νC=O frequencies. As the volume % of benzaldehyde increased, the interaction of solute/solute increased and C=O frequency shifted to the lower frequency. While in dilute solution the frequency shifts reflect the solvent-solute hydrogen bond strength. By increasing the concentration of benzaldehyde from 1% to 80% the red shift change of νC=O in nonpolar solvents was much larger than in polar solvents except in C₂H₅OH.

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A Statistical Thermodynamic Study on the Conformational Transition of Oligopeptide Multimer

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The conformational transition of oligopeptide multimer, -(HPPHPPP)n-, is studied (H : hydrophobic amino acid, P : hydrophilic amino acid). The helix/coil transitions are detected in the multimer. The transition depends on the number of amino acid in the sequence, the concentration of the oligopeptide, and temperature which affects helix stability constant (ξ) and hydrophobic interaction parameter (w_j). In the thermodynamic equilibrium system $jA \to A_j$ (where A stands for oligopeptide monomer), Skolnick *et al.*, explained helix/coil transition of dimer by the matrix method using Zimm-Bragg parameters ξ and σ (helix initiation constant). But the matrix method do not fully explain dangling H-bond effects which are important in oligopeptide systems. In this study we propose a general theory of conformational transitions of oligopeptides in which dimer, trimer, or higher multimer coexists. The partition of trimer is derived by using zipper model which account for dangling H-bond effects. The transitions of multimers which have crosslinked S-S bonds or long chains do not occur, because they keep always helical structures. The transitions due to the concentration of the oligopeptides are steeper than those due to the chain length or temperature.

Introduction

The structure and folding of proteins have been actively studied after Pauling and Corey *et al.*[1] discovered α-helical structure of protein in 1951. To understand the folding mechanism of protein and its biological activity, it is necessary to have a knowledge of the spatial coformations. X-ray diffraction has been successful in elucidating the three dimensional structure.[2] However, these crystallographic analyses are quite laborious, expensive, and time consuming. Futhermore many membrane and ribosomal proteins as well as histones, have not yet yielded suitable crystals, so other approaches such as theoretical methods must be explored to give structural information on the basis of experimental data and statistical mechanics.

The theoretical studies on the secondary structure of protein have been done by Chou and Fasmann *et al.*[3] From the tertiary structures of protein solved by X-ray crystallography, they obtained the probabilities of amino acid sequences for α-helical structures, β-sheet, β-turn, and random coils. A study on α-helical structure is more important than any other secondary structures, as α-helical structure amounts up to 80% of many proteins. The regularity of α-helical structure enables a theoretical model to be constructed. As the mean length of α-helix is shorter than 30 residues[4~8] of amino acids, the thermodynamic properties of α-helix in that range are important. Dangling H-bond which exists in the end of α-helix is not important in a long chain, but it must be considered in a short chain in thermodynamic study.

Zimm-Bragg parameters (helix initiation constant and helix stability constant) are insufficient to explain the thermodynamic phenomena of proteins. α-helical structure is determined not only by α-helical H-bonds but also by the species of amino acids and the tertiary interactions surrounding α-carbons of amino acids.[9] The probabilities of amino acids to form α-helices depend on whether they are located inside or surface of protein. The fractional helicity of oligopeptide multimer increases to unity as the concentration of oligopeptide increases.

Skolnick *et al.* derived the partition function of dimer using the matrix method which Zimm *et al.*,[10] and Lifson *et al.*[11] have used and the thermodynamic properties[12~17] of polypeptide. However, this method can not explain dangling H-bond. In this study the thermodynamic functions of polypeptides system, where chain multimers coexist, are derived using zipper model. By this method helix/coil transitions of oligopeptide where dangling H-bonds are important can be well explained.

Theory

The theoretical Study of the conformational Transition of uncross-linked Multimers. Polypeptides-(HPPHPPP)n- are presented as dimer, trimer, tetramer, or higher multimer[18~21] (H : hydrophobic amino acid, P : polar amino acid). In the case of dimer, hydrophobic amino acids are located in a and d position of helical wheel and hydrophobic interactions[22~26] between a-d', a'-d stabilize dimer (Fi-