Fermi Resonance and Solvent Dependence of the νC=O Frequency Shifts of Raman Spectra: Cyclohexanone and 2-Cyclohexen-1-one

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The carbonyl stretching vibration, νC=O of 2-cyclohexene-1-one, is in Fermi resonance with a combination tone. The amount of Fermi resonance interaction between these two modes is dependent upon the amount of solute/solvent interaction due to hydrogen bonding between the carbonyl oxygen and the solvent proton. The corrected νC=O frequency of 2-cyclohexene-1-one occurs at a lower frequency than the observed νC=O mode of cyclohexanone, possibly caused by expanded conjugation effects. The carbonyl stretching modes of cyclic ketones were also affected by interaction with the ROH/CCl_4 mixed solvent system.

Keywords : Fermi resonance, Raman spectra, Cyclohexanone.

Introduction

The carbonyl stretching mode, νC=O of cyclopentanone has been reported to be in Fermi resonance with a combination tone.[1-3] If a fundamental vibration and an overtone or a combination of other vibrations in a molecule are comparable in frequency, they interact by the anharmonic part of the Hamiltonian when allowed by symmetry. The results are frequency shifts and mixings of the wavefunctions with corresponding changes in the IR and Raman activities. Jones *et al.* attributed the presence of the doublet in the νC=O region of the IR spectrum of coumarin to Fermi resonance of νC=O with an overtone of a lower-lying fundamental.[4]

The carbonyl stretching mode, νC=O, is known to be affected by solute/solvent interaction.[5-13] The study of the effect of solute/solvent interaction and solute/solute interaction is of interest to solution chemists. In this work, a Raman spectroscopic study has been performed on cyclohexanone and 2-cyclohexene-1-one in various solvents in order to have further insight into the solute/solute interaction.

Experimental Section

The Raman spectroscopic apparatus used in this study is a Spex model 1403 equipped with a 0.85 m Double monochromator and a RCA C31034 PM tube detector. A 50 mW laser beam with a 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. The Raman spectra were recorded using an IBM compatible 486 PC along with SPEX DM 3000^R software. All of the spectra shown were obtained by a single scan at a rate of 0.2 cm^{-1}/0.3 sec with slit settings of 400/400/400/400 m. 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 spectra of cyclohexane and 2-cyclohexen-1-one are shown in Figure 1. In Figure 1, a νC=O band of cyclohexanone is observed at 1709.0 cm^{-1} while 2-cyclohexene-1-one exhibits bands at 1669.4 and 1682.4 cm^{-1} in the carbonyl stretching region of the spectrum. Further, a lower frequency band has more intensity than the higher one. The band of

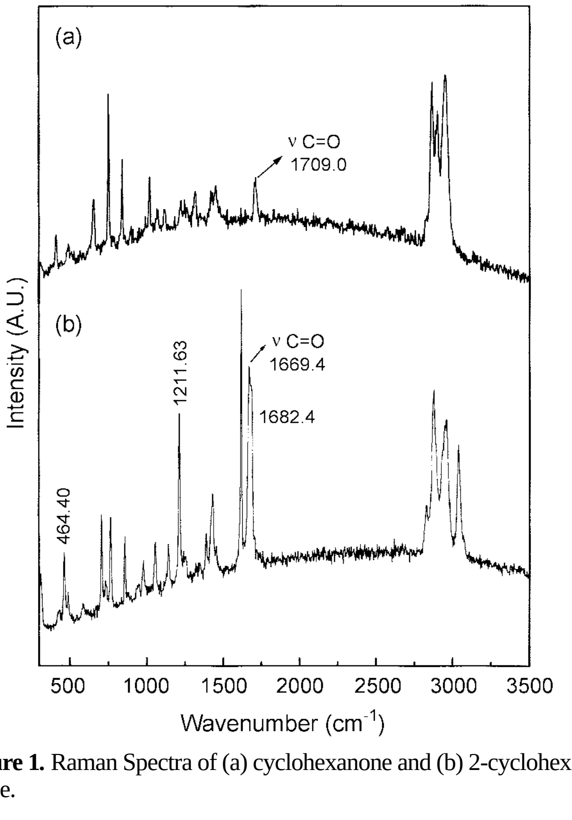

Figure 1. Raman Spectra of (a) cyclohexanone and (b) 2-cyclohexen-1-one.

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νC=O with a combination tone is observed in the 1665.6-1684.4 cm^{-1} region. The combination tone may be the ring breathing with C=C skeletal deformation. The carbonyl stretching vibration mode, νC=O, of 2-cyclohexene-1-one is in Fermi resonance with a combination tone. The amount of Fermi resonance interaction between these two modes is dependent upon the amount of solute/solvent interaction. The method of Langseth and Lord[8-9] to correct Fermi resonance was used to obtain the unperturbed νC=O frequency in each solvent.

$$\overline{\nu}_A^0 \cong \frac{(\overline{\nu}_A + \overline{\nu}_B)}{2} + \frac{(\overline{\nu}_A + \overline{\nu}_B)}{2}\left[\frac{I_A - I_B}{I_A + I_B}\right],$$

$$\overline{\nu}_B^0 = \frac{(\overline{\nu}_A + \overline{\nu}_B)}{2} + \frac{(\overline{\nu}_A + \overline{\nu}_B)}{2}\left[\frac{I_A - I_B}{I_A + I_B}\right]$$

$\overline{\nu}_A^0$: unperturbed fundamental vibration

$\overline{\nu}_B^0$: unperturbed overtone and combination tone

$\overline{\nu}_A$, $\overline{\nu}_A$: observed frequencies

I_A, I_B : intensity

Table 1. Raman data for uncorrected and corrected νC=0 frequencies of various volume % 2-Cyclohexen-1-one in various solvents

Volume	Solvent	AN	Observed[a]		Intensity			Corrected[b]	
			(1)	(2)	I(1)	I(2)	I(2)/I(1)	(1)	(2)
80%	Hexane	0.0	1670.6	1683.4	20903.4	20736.6	0.992	1677.97	1677.03
	Benzene	8.2	1672.0	1684.0	19328.6	18619.8	0.963	1677.89	1678.11
	Carbon tetrachloride	8.6	1671.6	1683.8	16859.1	17190.9	1.020	1677.76	1677.64
	Acetonitrile	14.3	1671.4	1684.0	14683.6	14371.2	0.979	1677.63	1677.77
	Benzonitrile	15.5	1670.8	1683.6	21323.6	20730.7	0.972	1677.11	1677.29
	Chloroform	23.1	1668.6	1683.2	19251.7	18639.1	0.968	1675.78	1676.02
	Ethyl alcohol	37.1	1668.0	1683.4	19216.3	18665.4	0.971	1675.59	1675.81
	Methyl alcohol	41.3	1665.6	1684.4	16335.7	15220.9	0.932	1674.67	1675.33
	Δcm^{-1}							3.30	1.70
60%	Hexane	0.0	1672.6	1684.8	15025.7	14741.4	0.981	1678.64	1678.76
	Benzene	8.2	1671.8	1684.4	15236.0	16076.9	1.055	1678.27	1677.93
	Carbon tetrachloride	8.6	1671.6	1684.6	12731.0	13082.9	1.028	1678.19	1678.01
	Acetonitrile	14.3	1672.6	1683.8	15500.6	15664.6	1.011	1678.03	1677.97
	Benzonitrile	15.5	1671.4	1684.2	19084.5	19065.2	0.999	1677.80	1677.80
	Chloroform	23.1	1668.0	1685.0	12537.4	10949.1	0.873	1675.70	1676.70
	Ethyl alcohol	37.1	1665.6	1684.6	14743.7	13638.9	0.925	1674.73	1675.47
	Methyl alcohol	41.3	1664.6	1684.8	12385.2	11109.1	0.897	1674.15	1675.25
	Δcm^{-1}							4.49	3.51
40%	Hexane	0.0	1673.0	1686.0	15436.9	17162.9	1.111	1679.84	1679.16
	Benzene	8.2	1673.0	1684.6	11136.9	12424.3	1.116	1679.12	1678.48
	Carbon tetrachloride	8.6	1672.8	1685.6	9609.5	10502.0	1.093	1679.48	1678.92
	Acetonitrile	14.3	1672.8	1685.2	12282.6	12037.6	0.980	1678.94	1679.06
	Benzonitrile	15.5	1672.8	1684.4	9860.0	10091.4	1.023	1678.67	1678.53
	Chloroform	23.1	1667.6	1684.6	12284.3	10947.1	0.891	1675.61	1676.59
	Ethyl alcohol	37.1	1664.6	1686.2	10776.6	9032.9	0.838	1674.45	1676.35
	Methyl alcohol	41.3	1663.4	1686.6	10668.9	8211.4	0.770	1673.49	1676.51
	Δcm^{-1}							6.35	2.65
20%	Hexane	0.0	1674.0	1687.4	8227.9	10323.3	1.255	1681.46	1679.94
	Benzene	8.2	1673.6	1685.6	5356.6	7008.3	1.308	1680.40	1678.80
	Carbon tetrachloride	8.6	1673.0	1686.4	6306.4	7869.3	1.248	1680.44	1678.96
	Acetonitrile	14.3	1673.8	1686.0	7604.1	7482.1	0.984	1679.85	1679.95
	Benzonitrile	15.5	1673.2	1684.4	7218.0	7626.6	1.057	1678.95	1678.65
	Chloroform	23.1	1667.4	1684.8	9509.1	8261.1	0.869	1675.49	1676.71
	Ethyl alcohol	37.1	1664.2	1687.0	5083.4	4094.9	0.806	1674.37	1676.83
	Methyl alcohol	41.3	1663.2	1687.2	5216.9	3742.9	0.718	1673.23	1677.17
	Δcm^{-1}							8.23	2.77
	Neat liquid		1669.4	1682.4	11365.9	10932.9	0.962	1675.77	1676.03

[a]Observed = the observed wavenumber. [b]Corrected = the corrected wavenumber for Fermi resonance

The corrected νC=O frequency of 2-cyclohexene-1-one are given in Table 1. The corrected νC=O frequency is 1675.77 cm^{-1} for pure 2-cyclohexene-1-one. In the case of Fermi resonance, both bands result from mixtures of the νC=O and the combination tone. However, for group frequency purpose, one usually calls the stronger of the two bands the νC=O mode. The corrected νC=O mode of 2-cyclohexene-1-one occurs at lower frequency than that of cyclohexanone due to the conjugation effect. The introduction of a C=C bond adjacent to a carbonyl group results in the electron delocalization in the carbonyl and double bonds. This conjugation increases the single bond character of the νC=O bond and consequently, lowers its force constant resulting in the lower frequency of carbonyl absorption. The corrected νC=O frequency is 1677.97 cm^{-1} for 2-cyclohexene-1-one in solution with hexane. In other solvents, the corrected νC=O mode occurs at lower frequency as the AN (Acceptor Number)[10] values of solvents increase. The lowest νC=O mode corrected for Fermi resonance is 1674.67 cm^{-1} for 2-cyclohexene-1-one in methyl alcohol solution. The result was due to the intermolecular hydrogen bond formed between the proton of the solvent and the νC=O group of 2-cyclohexene-1-one. In case of polar solvents such as chloroform, ethyl alcohol and methyl alcohol, intermolecular hydrogen bonding occurs between the carbonyl group and the solvent proton such as ROH : O=C or Cl_3CH : O=C. The stronger the intermolecular hydrogen bond between solute and polar solvent, the more νC=O shifts to lower frequency.

In addition, the corrected νC=O frequencies of 2-cycloexene-1-one for various volume % solution in each solvent are shown in Table 1. As the concentration of 2-cycloexene-1-one decreased, the corrected νC=O frequencies in nonpolar solvents (hexane, benzene, carbon tetrachloride, acetonitrile and benzonitrile) increased while the corrected νC=O frequencies in polar solvents (chloroform, ethyl alcohol and methyl alcohol) decreased. These tendencies were mainly due to solute/solvent and solute/solute interactions. In nonpolar solvents, solute/solute interaction was stronger than solute/solvent, but in polar solvents, solute/solvent was weaker than solute/solute. The plots of data in Table 1 are shown in Figure 2 and 3. As shown in Figure 3, the solvent AN values do not correlate well with the carbonyl stretching vibrations of 2-cyclohexene-1-one. The AN values are not a precise measure of solute/solvent interaction for all solutions. Factors such as intermolecular hydrogen bonding between solute and solvent and the differences between molecular geometry of the solutes and solvents most likely account for differences in the solute/solvent interaction for different solutes in the same solvents.

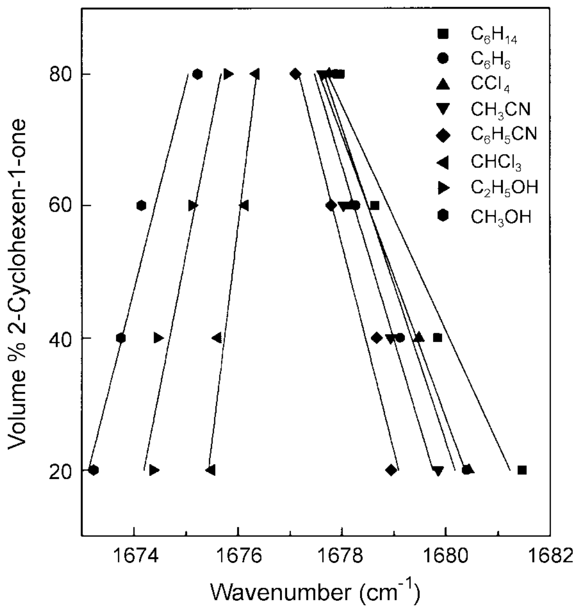

Figure 2. The plots of νC=O frequencies for 2-cyclohexen-1-one vs its volume % in various solvents.

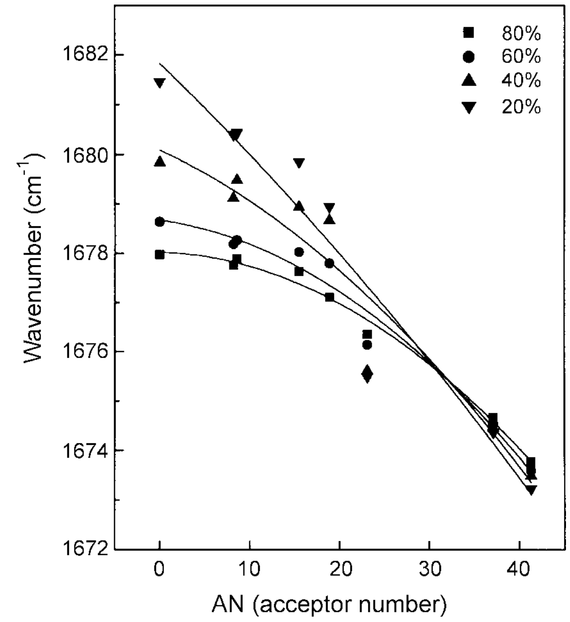

Figure 3. The plots of νC=O frequencies for 80, 60, 40 and 20 volume % solutions of 2-cyclohexen-1-one vs. the acceptor number (AN) of the solvent.

The Raman data of the νC=O frequencies of cyclohexanone for various volume % in each solvent are given in Table 2. When the volume % of cyclohexanone in each solvent decreased, the νC=O frequency shift were similar to the tendency of 2-cyclohexene-1-one. In the same series of solvents, the strength of hydrogen bonding between solute and solvent for cyclohexanone is larger than 2-cyclohexene-1-one, progressing in the series of solvents from nonpolar solvents through polar solvents. The plots of data in Table 2 are shown in Figure 4 and 5.

In Figure 2 and 4, red shifts of νC=O were observed in non-polar solvents as the volume % of solutes increased, while blue shifts were observed in polar solvents. These shifts 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.[14,15] In polar solvents, the blue shift is due to the reduced amount of hydrogen bonds between the solute carbonyl groups and solvent hydrogens as the volume % of solute

Table 2. Raman data of corrected νC=O frequencies for volume % cyclohexanone in various solvents

Volume % / Solvent	AN	80 (cm^{-1})	60 (cm^{-1})	40 (cm^{-1})	20 (cm^{-1})	Δcm^{-1}
Hexane	0.0	1708.6	1710.6	1712.6	1714.6	6
Benzene	8.2	1708.2	1709.8	1710.4	1712.2	4
Carbon tetrachloride	8.6	1708.0	1709.4	1710.2	1712.0	4
Acetonitrile	14.3	1707.0	1707.6	1708.4	1708.8	1.8
Benzonitrile	15.5	1706.2	1706.6	1708.0	1708.6	2.4
Chloroform	23.1	1705.2	1705.0	1704.8	1704.6	0.6
Ethyl alcohol	37.1	1704.4	1704.0	1703.6	1703.2	1.2
Methyl alcohol	41.3	1703.8	1703.0	1702.6	1702.4	1.4
Δcm^{-1}		4.8	7.6	10.0	12.2	
Pure			νC=O	1705.8		

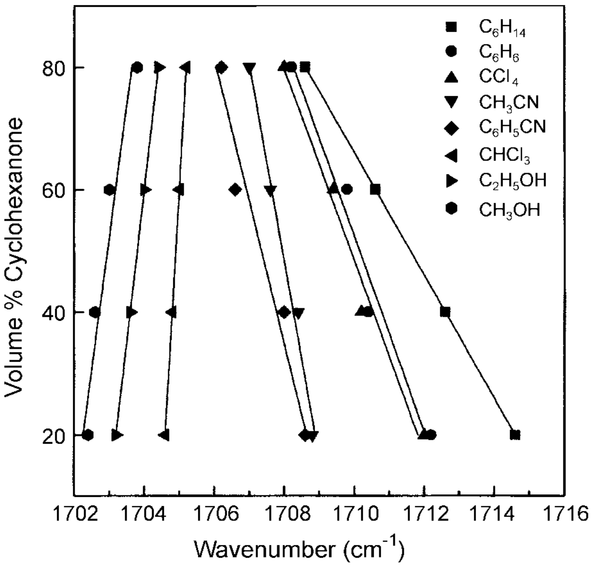

Figure 4. The plots of νC=O frequencies for cyclohexanone *vs.* its volume % in various solvents.

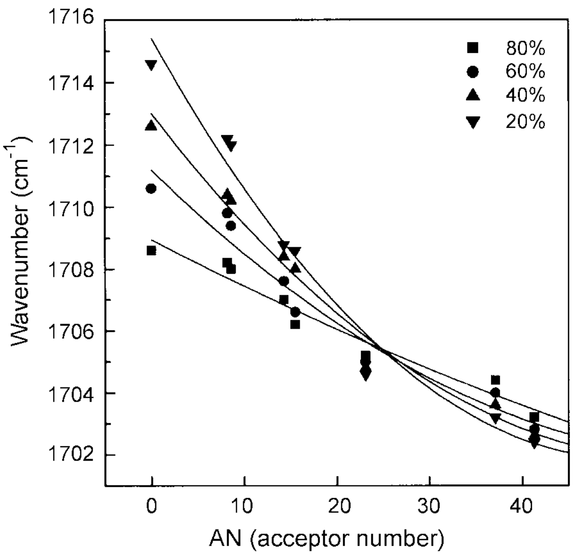

Figure 5. The plots of νC=O frequencies for 80, 60, 40and 20 volume % solutions of cyclohexanone *vs.* the acceptor number (AN) of the solvent.

Table 3. Raman data for νC=O frequencies of 2-cyclohexen-l-one and cyclohexanone in ethyl alcohol and/or CCl_4 solutions

Volume % C_2H_5OH/CCl_4	Cyclohexanone (cm^{-1})	2-Cyclohexen-1-one (cm^{-1})
100	1702.6	1675.15
80	1702.8	1675.63
60	1704.2	1675.78
40	1706.4	1676.22
20	1707.6	1678.22
0	1708.8	1678.51
Δcm^{-1}	6.2	3.27

increased. However, in nonpolar solvents, the red shift is mainly due to the dipole-dipole interactions plus weak hydrogen bonds between the solutes. The strength of interactions between solutes-solvents and solutes-solutes are as follows:

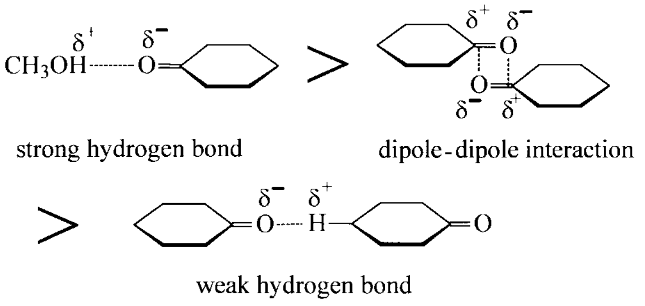

Table 3 lists the Raman data of the corrected C=O frequencies for 2-cyclohexene-1-one and cyclohexanone in an ethyl alcohol and/or CCl_4 mixed solution. As the volume % C_2H_5OH/CCl_4 increased, the corrected C=O frequencies decreased. The corrected carbonyl stretching mode shifts to lower frequency mode in the range of 60-100 volume % whereas in the range of 20-40 volume % shifts this mode to higher frequency. As the volume % of ethyl alcohol with intermolecular hydrogen bonding decreased, a fundamental frequency passes a higher frequency and the maximum resonance interaction occurs. The two components possess equal or near equal intensities. Continuous variation of volume % shifts the more intense component away from the weaker component, thus causing a decrease in the degree of

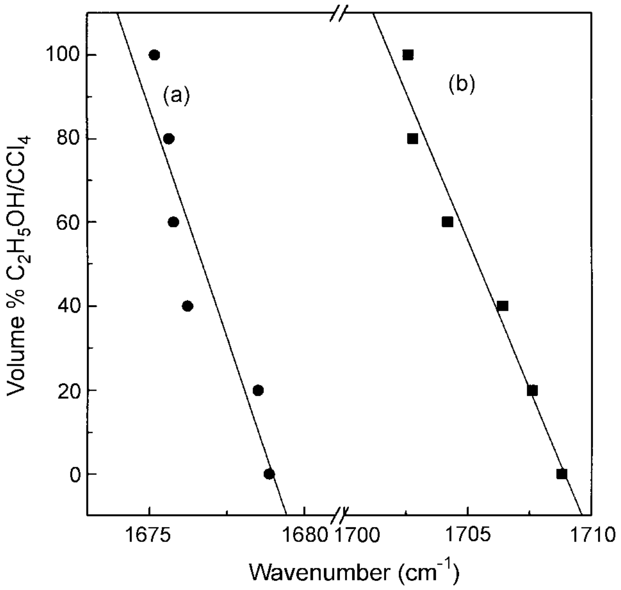

Figure 6. The plots of νC=O frequencies for (a) 2-cyclohexen-1-one and (b) cyclohexanone in C_2H_5OH and/or CCl_4 *vs*. the volume % in C_2H_5OH/CCl_4.

resonance interaction and different intensities for the two components. Consequently, the νC=O frequency decreases through an increase of volume % C_2H_5OH/CCl_4 as a result of the hydrogen bonding between proton of C_2H_5OH and carbonyl oxygen. And, Table 3 lists the Raman data of νC=O frequencies for cyclohexanone in ethyl alcohol and/or CCl_4 mixed solution. As the volume % of C_2H_5OH/CCl_4 increased, the corrected νC=O frequencies decreased. These results suggest that intermolecular hydrogen bonds make equilibrium between ROH and carbonyl oxygen of cyclohexanone. Figure 6 shows the corrected νC=O frequencies of 2-cyclohexene-1-one and cyclohexanone with change of volume % C_2H_5OH/CCl_4. The corrected νC=O frequency of 2-cyclohexene-1-one occurs at lower frequency than that of cyclohexanone. These data have been attributed to the conjugation effect.

Conclusion

The carbonyl stretching vibration, νC=O, of cyclic ketones was observed in 1673.2-1714.6 cm^{-1} region and that of 2-cyclohexene-1-one is in Fermi resonance with a combination tone. The corrected n C=O frequency of 2-cyclohexene-1-one occured about a 33.2 cm^{-1} lower frequency than that of cyclohexanone, possibly owing to expanded conjugation effects. In various solvents, the νC=O of cyclic ketones decreased in frequency as the solvent polarity increased. The νC=O of cyclic ketones were shifted to a lower frequency in nonpolar solvents as the volume % of solute increased. On the other hand, the νC=O of cyclic ketones were shifted to higher frequency as the volume % of solute increased in polar solvents. In nonpolar solvents, the shift was due to dipole-dipole interaction between the carbonyl groups of solutes. In polar solvents, the shift was due to hydrogen bonding between the carbonyl group of solute and solvent proton. The carbonyl stretching modes of cyclic ketones were also affected by the solute/solvent interaction in mixed the solvent system.

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