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Raman Spectra of Compounds under Inversion Motions. IV. *N*-Methyl-2-pyrrolidone

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The Raman spectra of *N*-methyl-2-pyrrolidone in various states were measured. Remarkable changes in the spectrum of CH_2 bending vibrations were found besides a spectrum change of the skeletal vibrations. Normal vibration calculations and measurements regarding band-intensity changes associated with temperature changes suggest that a change of the ring conformation takes place in this molecule by hydrogen bonding to a nitrogen atom.

Former studies[1)] made it clear that hydrogen bonding to some kind of nitrogen atom causes the frequencies of the Raman bands of the skeltal-deformation vibrations to change remarkably, and the phenomenon was interpreted to be associated with an inversion at the nitrogen. In the present study, *N*-methyl-2-pyrrolidone was investigated from the point of view that the molecule may have a lower potential barrier for inversion at the nitrogen because of a tendency of the CONCC skeleton to form a plane by resonance and, therefore, might show a specific spectrum change due to hydrogen bonding to the nitrogen.

Experimental

Sample *N*-methyl-2-pyrrolidone was a commercial product from Tokyo Kasei Co. (grade GR). The Raman spectra were recorded on a Model R-800T Raman spectrometer (Japan Spectroscopic Co.) with an excitation effected by a Spectra Physics argon ion laser (Model 165) at 514.5 nm (300 mW). The depolarization ratio was measured with a system consisting of a half-wave plate, a lens, and a polarizer. Liquid samples at room temperature were measured with 0.3 ml Raman cells, while crystals, solutions, and pure liquids at lower temperatures were measured with an Oxford-type cryostat and liquid nitrogen. Experimental results are shown in Tables 1 and 2 and Figs. 1—3.

Normal Coordinate Treatment

Normal vibration calculations regarding the axial and equatorial conformers of *N*-methyl-2-pyrrolidone were carried out according to Wilson's GF matrix method[2)] by use of the Computation Center, University of Tokyo and the library programs BGLZ and LSMB. The molecular parameters used are: bond

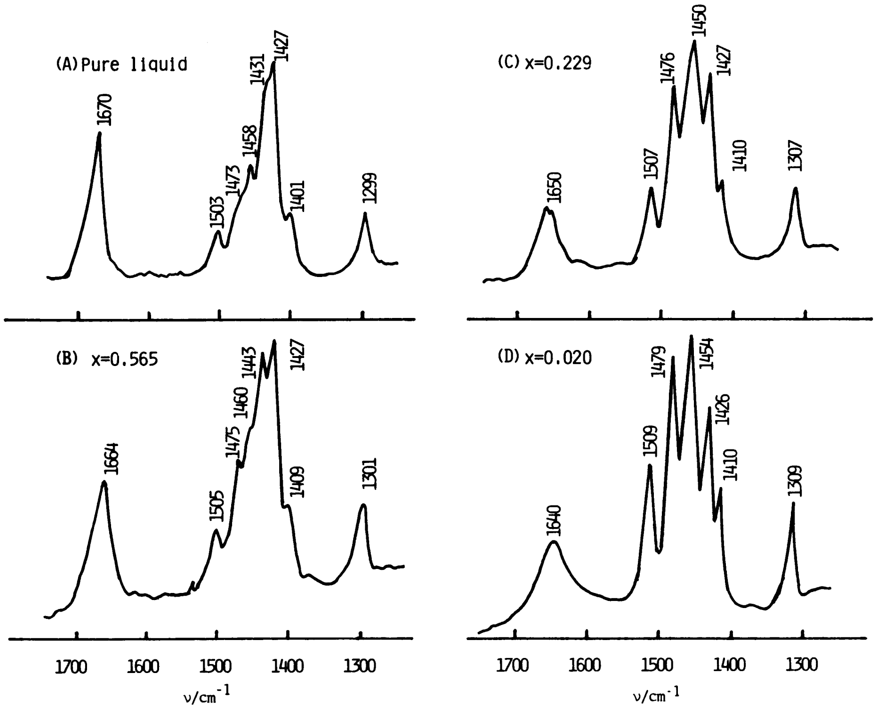

Fig. 1. Concentration dependence of spectra of *N*-methyl-2-pyrrolidone in aqueous solutions (x: mol fraction of *N*-methyl-2-pyrrolidone).

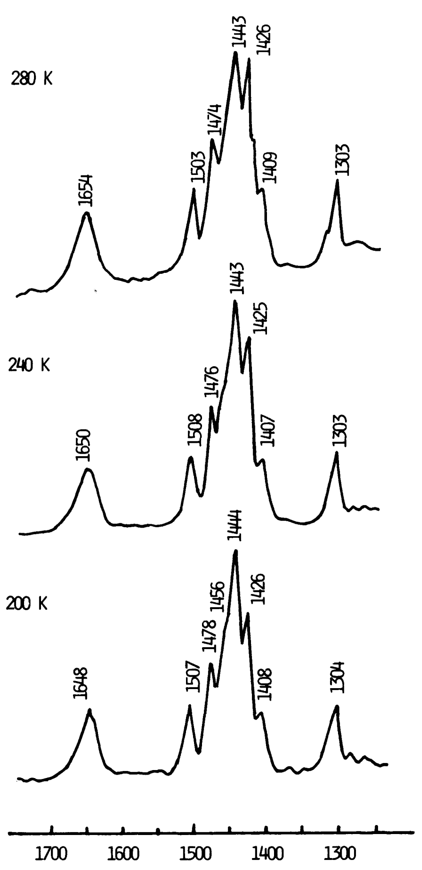

Fig. 2. Temperature dependence of spectra of *N*-methyl-2-pyrrolidone in an aqueous solution (mol fraction of *N*-methyl-2-pyrrolidone : 0.406).

lengths, r(N–CO)=1.48 Å, r(CH$_2$–CO)=1.53 Å, r(CH$_2$–CH$_2$)=1.54 Å, r(CH$_2$–CN)=1.53 Å, r(CH$_2$–N)=1.48 Å, r(C=O)=1.24 Å, r(N–CH$_3$)=1.49 Å, r(C–H)=1.09 Å; bond angles, (CH$_2$–N–CO)=100.8°, (CH$_3$–N–CO)=(CH$_2$–N–CH$_3$)=111.6°, (CH$_2$–CO–N)=(CH$_2$–CH$_2$–N)=105°, (CH$_2$–CH$_2$–CO)=(CH$_2$–CH$_2$–CH$_2$)=104°, (N–C=O)=(CH$_2$–C=O)=127.5°, and bond angles of CH$_3$ group=tetrahedral angles.[3,4] For the molecular models, an envelope structure for the five membered ring was used as in the case of *N*-methylpyrrolidine.[5] Most of the force constants used are those of *N*-methylpyrrolidine.[5] The result of the calculation is shown in Fig. 3.

Results and Discussion

Spectrum Change Associated with the State Change from Liquid to Solid. As shown in Table 1, no appreciable spectrum change was observed except for the change in the region, 100 cm^{-1}—250 cm^{-1} where several new bands of lattice vibrations appear in the spectrum of the solid, and also the appearance of some bands in the spectra of the solid, which were not clearly observed in the spectra of the pure liquid because of weakness and broadness. This shows that one kind of conformer exists both in the solid and liquid states.

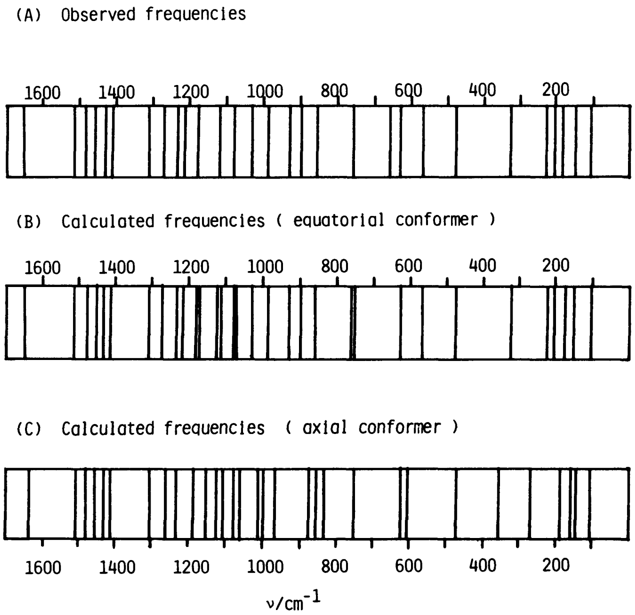

Fig. 3. Calculated frequencies of conformers of *N*-methyl-2-pyrrolidone compared with observed frequencies of pure liquid.

Spectra of Solutions for Non Hydrogen Bonding Solvents. The spectra of *N*-methyl-2-pyrrolidone in benzene, carbon tetrachloride, acetone, acetonitrile, and pyridine are almost the same as that of a pure liquid. Therefore, the conformer in these solutions is the same as that of a pure liquid. In Table 2, as a representative, the Raman bands of benzene solution are shown.

Spectrum Change Associated with Solution into Hydrogen Bonding Solvents. Change of Raman bands of skeletal deformation vibrations: The Raman bands at 310 cm^{-1} and 170 cm^{-1} in the spectra of a pure liquid shift to 325 cm^{-1} and 225 cm^{-1}, respectively, in spectra of solutions (refer to Table 1). A normal vibration calculation shows that these frequency shifts are not caused by a conformational change, equatorial conformer to axial conformer (refer to Fig. 3) and also that the former band is due to the vibrational mode of the C–N–C skeleton. These shifts, along with temperature dependence of intensities of these bands, suggest that the same kind of change of valence state of nitrogen atom (as described in former studies[1)]) also takes place in this molecule. Corresponding frequencies for solutions of formic acid, acetic acid or aqueous hydrochloric acid (refer to Table 2) confirm that the frequency change in aqueous solutions is due to conformational change arising from the change of valence state of nitrogen atom.

The band of pure liquid at 170 cm^{-1}, which is

Table 1. Raman spectra of *N*-methyl-2-pyrrolidone

Pure liquid			Solid		H_2O soln						CH_3OH soln		
					x=0.565			x=0.033					
ν	I	ρ	ν	I	ν	I	ρ	ν	I	ρ	ν	I	ρ
			105	7									
			150	13									
170	sh		178	25	190	sh							
			203	15	210	sh		225	sh				
			247	2									
310	48	0.53	308	100	313	40	0.56	325	32	0.44	319	28	0.49
			359	3									
			378	4									
472	11	0.55	473	17	472	9	0.66	475	8	0.62	475	7	0.59
			500	2									
564	6	0.47	567	11	563	6	0.67	569	6	0.44	561	7	0.39
617	60	0.36	619	89	618	62	0.40	623	57	0.36	617	63	0.32
657	8	0.63	649	14	656	8	0.75	660	8	0.70	660	8	0.68
746	100	0.09	748	58	746	100	0.11	753	86	0.10	744	94	0.09
			822	4									
850	28	0.10	842	31	851	32	0.17	856	39	0.18	850	35	0.13
895	5	0.40	894	7	895	6	0.53	896	8	0.47	895	6	0.25
925	97	0.10	923	83	925	99	0.10	932	100	0.07	925	6	0.25
			959	2									
938	9	0.33	983	11	983	12	0.34	988	17	0.38	985	.16	0.38
1022	17	0.62	1027	34	1024	19	0.65	1029	21	0.55			
1070	2	0.64	1065	7	1070	2	0.72	1073	3	0.73	1034*		
			1095	4									
1113	4	0.73	1111	14	1113	5	0.57	1118	6	0.73			
			1135	5									
			1145	3									
1174	1	0.67	1172	4	1175	2	0.61	1176	2	0.75	1107*		
											1152*		
1205	7	0.67	1206	13	1206	9	0.63						
								1214	11	0.48	1211	6	0.75
1224	15	0.75	1226	17	1225	18	0.69	1229	24	0.69	1224	13	0.75
1263	vw				1266	2	0.48						
1277	vw		1278	3									
1299	12	0.19	1298	8	1301	16	0.21						
								1308	21	0.23	1304	12	0.17
1316	1	0.20	1313	3							1316	5	0.15
					1321	3	0.40	1325	8	0.18			
			1328	4									
			1356	3									
			1369	3									
			1394										
1401	13	0.45	1404	14	1409	16	0.55						
								1412	23	0.32			
1427	43	0.56	1423	39	1427	48	0.60	1428	41	0.52	1427	45	0.56
1431	39	0.51											
			1442	37	1443	46	0.53				1448	97	0.45
1458	22	0.60	1458	14	1460	31	0.63	1456	56	0.45	1455	80	0.56
			1468	13									
1473	12	0.54	1476	16	1475	25	0.43	1480	52	0.34	1472	65	0.59
1503	8	0.58	1507	19	1505	12	0.37	1510	29	0.13	1501	23	0.61
			1659	23									
1670	30	0.13	1673	7	1664	24	0.27	1647	13	0.25	1665	13	0.31

ν: Raman shift frequency. I: Relative intensity. ρ: Depolarization ratio. *: Solvent band. x: Mol fraction of *N*-methyl-2-pyrrolidone.

TABLE 2. RAMAN SPECTRA OF *N*-METHYL-2-PYRROLIDONE IN SOLUTIONS

Pure liquid			C_6H_6 soln			CH_3COOH soln			HCl soln		
ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ
170	sh										
			228	sh							
						277	sh		275	sh	
310	48	0.53	310	52	0.48						
						325	31	0.60	330	16	0.76
									356	7	0.50
									419	4	0.67
									458	6	0.73
472	11	0.55	473	12	0.60	480	7	0.73	475	6	0.67
									506	5	0.25
564	6	0.47	565	8	0.69	565	7	0.75	558	9	0.64
617	60	0.36	*			*			618	71	0.48
657	8	0.63	658	10	0.74	662	11	0.75	642	27	0.70
746	100	0.09	746	92	0.09	749	97	0.09	746	59	0.09
850	28	0.10	853	63	0.41	855	sh		852	64	0.12
895	5	0.40	893	3	0.65	*			890	21	0.40
925	97	0.10	925	100	0.07	926	100	0.09	928	100	0.10
983	9	0.33		sh		985	17	0.41	982	41	0.56
1022	17	0.62	1024	30	0.39	1024	24	0.64	1023	31	0.69
1070	2	0.64	1074	4	0.42	1070	4	0.75	1066	6	0.50
1113	4	0.73	1108	3	0.48	1118	6	0.71	1113	8	0.76
1174	1	0.67	*			1170	3	0.44	1182	6	0.67
1205	7	0.60				1206	10	0.62	1207	7	0.61
1224	15	0.75	1221	19	0.65	1225	22	0.75	1228	30	0.75
1263	vw										
1277	vw					*			1276	6	0.50
1299	12	0.19	1298	12	0.20	1304	15	0.27			
1316	1	0.20				1315	6	0.42	1313	38	0.26
									1325	30	0.13
1401	17	0.42	1406	31	0.31						
						*			1415	77	0.48
1427	43	0.56	1426	52	0.58	*					
1431	39	0.51									
1458	22	0.60	1459	22	0.75				1453	48	0.69
1473	12	0.54	1474	20	0.57	1476	43	0.45	1474	57	0.56
1503	8	0.58	1502	9	0.61	1506	27	0.18			
						1637	26	0.20			
1670	30	0.13	1685	33	0.34						
									1702	42	0.29

ν: Raman shift frequency. I: relative intensity. ρ: depolarization ratio. *: solvent band.

assigned to C–C, C–N torsional modes by normal vibration calculation and, therefore, is caused by ring vibration, shifts by 55 cm^{-1} on hydrogen bond formation to nitrogen atom. This change of ring vibration associated with hydrogen bond formation is a discovery in the present study along with the following remarkable change of CH_2 bending vibrations.

Remarkable Change of Raman Bands of CH_2 Bending Vibration: As shown in Table 1 and Fig. 1, a remarkable spectrum change was observed for aqueous solutions in the region of 1400—1550 cm^{-1}. With a decreasing concentration of *N*-methyl-2-pyrrolidone, intensities of the bands at 1401 cm^{-1}, 1431 cm^{-1}, 1503 cm^{-1} decrease, while those of the newly observed bands at 1410 cm^{-1}, 1450 cm^{-1}, 1510 cm^{-1} increase, The band at 1458 cm^{-1}, 1473 cm^{-1} also increase their intensities. These bands are clearly assigned to the CH_2 bending vibrations. Usually, the CH_2 bending vibrations do not show any great changes, and such a change has not been reported so far. It is amazing that the CH_2 bending bands of the molecule change so much. The band at 1426 cm^{-1} decreases in intensity as the temperature decrease, while the band at 1443 cm^{-1} increases its intensity (refer to Fig. 2).

From the measurement of the intensity change, an enthalpy change of −2.0 kJ/mol was obtained, showing that the latter band is assigned to the conformer having a smaller enthalpy value and therefore, it is due to the hydrogen-bonded conformer. Considering the change of the band at 170 cm^{-1}, which shows a change in ring conformation by hydrogen bonding, the above change of the CH_2 vibration bands suggests that the shape of the ring in the molecule changes by hydrogen bonding to a nitrogen atom, and the electronic state of the carbon atom of the CH_2 groups changes to cause a remarkable change in the CH_2 vibrations. As the skeleton of 2-pyrrolidone was reported to take a planar conformation,[3] the real molecular ring of *N*-methyl-2-pyrrolidone might be also an almost planar ring a little different from the envelope model, which is commonly approved for five-membered ring and used in the present calculation, and nitrogen atom might be nearly in sp^2 state. The above spectrum change may be caused by the change of the sp^2 state of nitrogen into an sp^3 state by hydrogen bond formation.

For solutions for formic acid, acetic acid, aqueous hydrochloric acid, where a proton is attached to the nitrogen atom to form an sp^3 state nitrogen atom, only three bands appear at ≈1415 cm^{-1}, ≈1453 cm^{-1} and ≈1474 cm^{-1}, which correspond to the bands at ≈1410 cm^{-1}, ≈1450 cm^{-1}, and ≈1477 cm^{-1} increasing intensities in aqueous solutions. This is more evidence that the change in aqueous solutions may be a state change of the nitrogen atom from sp^2 to sp^3.

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