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Molecular Deformation Caused by Hydrogen Bonding. 1,3-Dimethylurea

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Synopsis. Raman spectra of 1,3-dimethylurea were measured for the crystalline state, acetone (proton acceptor) solution and water and methanol (proton donors) solutions. Remarkable differences were observed among the spectra of the aqueous solution and those of the acetone solution and the crystal. The difference is interpreted as due to the molecular deformation caused by hydrogen bonding.

Urea dissolves almost freely into water to form a solution similar to an ideal solution.[1] It is expected that the interaction of urea molecule with water molecules in an aqueous solution is strong enough to cause deformation of some parts of molecules associated with a change of the valence state of nitrogen atom (sp^2 state→sp^3 type state) by hydrogen bonding to the atom. This deformation in aqueous solutions, if it exists, may be found most effectively by Raman spectroscopy. A recent unpublished study of Raman spectra of urea in aqueous solutions by one of the present authors suggested the presence of the deformation, but the experimental results were not clear enough to be certain about it. In the present study, a related molecule, 1,3-dimethylurea, which is expected to show considerable frequency changes of its skeletal deformation vibrations associated with molecular deformation, was examined by Raman spectroscopy.

Experimental

Commercial 1,3-dimethylurea (grade EP, wako Chemicals Co., Ltd.) was used for preparation of the sample solutions: aqueous solution (x=0.065); acetone solution (x=0.096); methanol solution (x=0.176); water-heavy water solution (x=0.151, x_{D_2O}=0.412, x_{H_2O}=0.437), heavy water solution of 1,3-dimethylurea-d_2 (x=0.113), where x denotes mol fraction of 1,3-dimethylurea or 1,3-dimethylurea-d_2. The heavy water was purchased from Merck Co., Ltd. (99.75%). Raman spectra were recorded on a Model 800T Raman Spectrophotometer (Japan Spectroscopic Co., Ltd.) using the excitation line of 514.5 nm (300 mW) of a Spectra Physics argon ion laser (model 165). Spectra of solutions were obtained by use of 0.3 ml Raman cells, while those of the crystal were obtained with a sample disc. The spectra were obtained under four time accumulations and with the resolution of 5 cm^{-1}.

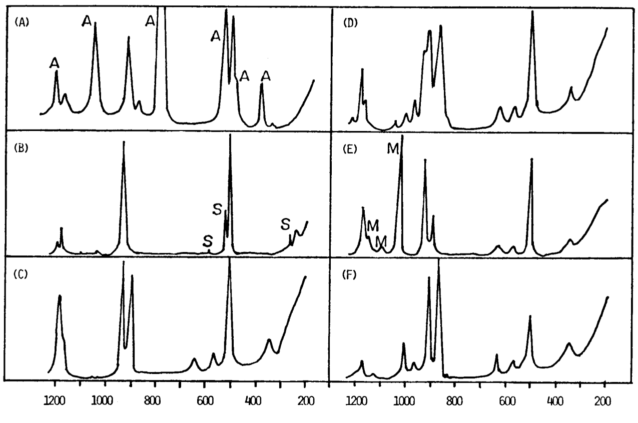

Fig. 1. Raman spectra ($I_{//}$) of 1,3-dimethylurea and 1,3-dimethylurea-d_2.
(A) Acetone solution, A: acetone band, (B) crystal, s: spontaneous emission line, (C) aqueous solution, (D) water–heavy water solution, (E) methanol solution, M: methanol band, (F) 1,3-dimethylurea-d_2 in heavy water.

Results and Discussion

In the following discussion, refer to Table 1 and Fig. 1. Observed Raman bands of crystalline 1,3-dimethylurea are consistent with previous works.[2–4] These bands persist in the spectrum of the compound in acetone (proton acceptor), while a new band having lower intensity appears at 875 cm^{-1}. Since the Raman bands of the crystal of 1,3-dimethylurea in the region below 1000 cm^{-1} are due to skeletal vibrations,[3] the presence of the band at 875 cm^{-1} suggests that another species, having a molecular skeleton different from that in the crystal, is generated in the solution. However, the abundance of the species is very low, because the relative intensity of the band is very weak. For the aqueous solution, a very intense band at 891 cm^{-1} and three other bands at 353 cm^{-1}, 573 cm^{-1}, and 643 cm^{-1} appear, and the same is the case for the methanol solution. Moreover, it was confirmed that the relative intensities of the four bands increase as the mol fraction of water or methanol (proton donor) in the solutions increases. Considering the remarkable spectrum change associated with solution, these four bands may be due to molecules deformed by being hydrogen bonded or due to the skeletal vibrations of non-deformed molecules, which include NH deformation modes and, therefore, are expected to change their frequencies considerably by hydrogen bond formation. The latter explanation is not reasonable, because the spectra of 1,3-dimethylurea in water–heavy water solution show that the frequencies of these four bands do not change much by *N*-deuteration. The band at 891 cm^{-1} forms a pair with the band of the crystal at 932 cm^{-1}, which is assigned to a coupled vibration of the CH_3–N stretching mode and the CH_3 rocking mode.[3] The band at 643 cm^{-1} and 573 cm^{-1} exist in the spectra of aqueous solutions instead of the band of the crystal at 510 cm^{-1}, which is assigned to a skeletal deformation vibration of the CH_3–NH–CO–N skeleton.[3] The band at 353 cm^{-1} forms a pair with the band of the crystal at 244 cm^{-1}, which is assigned to a skel-

Table 1. Observed shift frequencies of raman bands of 1,3-dimethylurea and 1,3-dimethylurea-d_2 (in cm^{-1})

Crystal		Aq soln			Acetone soln			Methanol soln			H_2O-D_2O soln			1,3-dmu-d_2 in D_2O		
ν	I	ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ
244	6	?	sh	?	?	sh	?	?	sh	?	?	sh	?			
		353	15	0.16	343	6	0.50	348	9	0.20	350	16	0.32	350	8	0.15
510	100	510	100	0.14	506	100	0.31	506	100	0.14	504	100	0.18	503	51	0.13
		573	12	0.29				572	5	0	572	13	0.30	570	7	0.30
		643	11	0.15				640	6	0	635	17	0.17	635	17	0.14
											840	sh	?	840	3	?
		891	86	0.04	875	20	0.31	890	42	0.42	870	85	0.06	870	100	0.04
932	93	930	99	0.05	924	76	0.07	926	95	0.04	915	82	0.06	910	83	0.04
											925	sh	?			
											968	25	0.14	968	14	0.12
											1007	10	0	1008	30	0
1043	2	1033	1	?				1035*	?	?	1044	5	0.14			
		1052	1	?							1055	sh	?			
														1130	5	0.30
		1161	11	0.14				1155*	5	0.40						
1179	22	1176	68	0.06	1175	31	0	1175*	47	0.33	1175	52	0.10	1175	17	0.09
1195	11	?	sh	?	?	sh	?	?	sh	?	?	sh	?			
														1210	5	0.10

ν: Shift frequency below 1220 cm^{-1}, I: relative intensity, ρ: depolarization ratio, *: overlapped by solvent band, 1,3-dmu-d_2: 1,3-Dimethylurea-d_2.

etal vibration of CH_3–NH–C skeleton.³⁾ Thus, these four bands are interpreted as generated by deformation of the CH_3–NH–C skeleton. Therefore, it is most probable that 1,3-dimethylurea undergoes molecular deformation when it acts as a proton acceptor at its nitrogen atom. But the presence of the band at 875 cm^{-1} in the spectrum of acetone (proton acceptor) solution seems to be contradictory with our explanation, even though it is very weak. However, this band may be ascribed to the molecules whose CH_3–NH–C skeletons are deformed by the N–H..N hydrogen bonding between 1,3-dimethylurea molecules.

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