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Temperature Dependence of Raman Spectra of Pyridine in Hydrogen Bonding Solvents

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Raman spectra of pyridine in solvents of various hydrogen bonding powers were recorded and frequency shifts of some bands were measured. With methanol as solvent, Raman spectra recorded at temperatures between 128 and 293 K exhibit a remarkable change with temperature. Results are interpreted on the basis of possible existence of a $\sigma\pi$-complex.

It was found by Takahashi *et al.*,[1] that some infrared bands of pyridine will shift to higher frequencies by its hydrogen bonding with solvents. They ascribed the frequency shifts to formation of σ-complexes (one-to-one and one-to-two complexes) by hydrogen bonding to the nitrogen atom of pyridine, and also to change in state of electrons in the molecule. On the other hand, Stidham and DiLella[2] measured frequency shifts of Raman bands of pyridine in various hydrogen bonding solvents. Infrared spectral change due to change in pyridine concentration in aqueous solution was investigated by Takahashi *et al.*,[1] but no works have been done on change in the above mentioned bands with temperature, although a temperature dependence of infrared spectra of hydrogen-bonded pyridine at 3 μ region was reported by Wolff *et al.*[3] On the other hand, a series of recent studies[4—7] on one-to-one σ-complexes by *ab initio* molecular orbital calculation made it clear that the π electron density on the nitrogen atom in the complexes is larger than that in pyridine itself,[8] and, therefore, existence of $\sigma\pi$-complex, in which a molecule is hydrogen-bonded to a one-to-one σ-complex by π-bonding, is probable. If $\sigma\pi$-complex coexists with one-to-one σ-complex, some peculiar temperature dependence of Raman spectra of pyridine in methanol is expected. In the present study, Raman spectra of pyridine in methanol were measured at various temperatures, and results were examined along with those of Raman spectral measurements at various concentrations, with the possibility of formation of $\sigma\pi$-complex taken into consideration.

Experimental

Raman spectra of pyridine and its aqueous and methanol solutions at various concentrations and those of pyridine in other hydrogen bonding solvents were measured. For a methanol solution (a mixture of pyridine and methanol in a mole ratio of 1 to 0.526), Raman spectra were measured at various temperatures between 128 and 293 K. Raman spectra of solutions at room temperature were measured using 0.3 ml Raman cells, while those at lower temperatures were measured by use of an Oxford-type cryostat using liquid nitrogen for cooling. Raman spectra were recorded on a Model R-800T Raman Spectrophotometer (Japan Spectroscopic Co., Ltd.) and the 514.5 nm line (300 mW) of a Spectra Physics argon ion laser (model 165).

Results and Discussion

(a) Raman Spectral Change Associated with Concentration Change. Change in spectra of pyridine in its aqueous solution with concentration is shown in Figs. 1, 2, and 3, in comparison with spectra of pure pyridine ((A) in the figures). In Figs. 1(B), (C), and (D), with decreasing concentration of pyridine, the intensity of the band at 1585 cm^{-1} (Fig. 1(B)) decreases and a new band at 1591 cm^{-1} (Fig. 1(B)) increases its intensity. At lower concentrations (Fig. 1(D)), the former almost disappears and changes into the band at 1594 cm^{-1} (Fig. 1(D)). This change confirms that the band at 1585 cm^{-1} forms a couple with the band at 1591 cm^{-1} (Fig. 1(B)), as the authors of Refs. 1 and 2 described. The reason why the intensity of the band at 1576 cm^{-1} (Fig. 1(B)) is not affected much by concentration change of pyridine is that a new band appears at 1578 cm^{-1} increasing its intensity with decreasing concentration of pyridine. In the same way as Fig. 1, Figs. 2 and 3 show that the bands at 998 and 992 cm^{-1} (Fig. 2(B)) and those at 612 and 605 cm^{-1} (Fig. 3(B)) form two couples. The

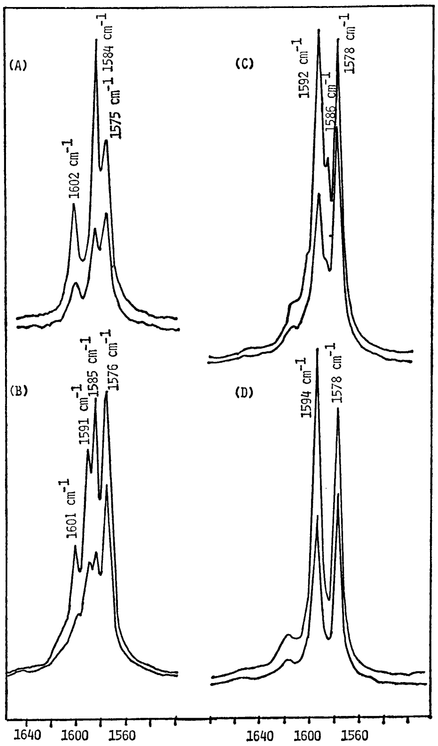

Fig. 1. Raman spectra (1540—1640 cm^{-1}, $I_{//}$ and $I_{\perp}$) of aqueous solutions of pyridine at room temperature. (A): Pyridine, (B): $X_P=0.746$, (C): $X_P=0.574$, (D): $X_P=0.214$, X_P: mole fraction of pyridine.

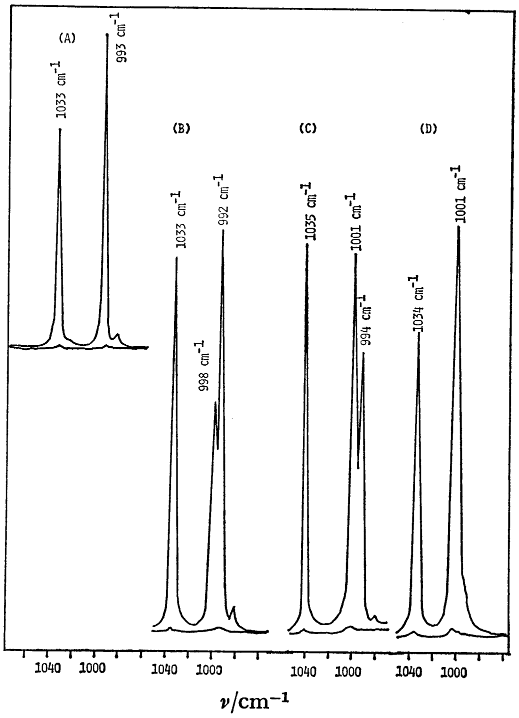

Fig. 2. Raman spectra (980—1060 cm^{-1}, $I_{//}$ and $I_{\perp}$) of aqueous solutions of pyridine at room temperature. (A): Pyridine, (B): $X_P=0.746$, (C): $X_P=0.574$, (D) $X_P=0.214$.

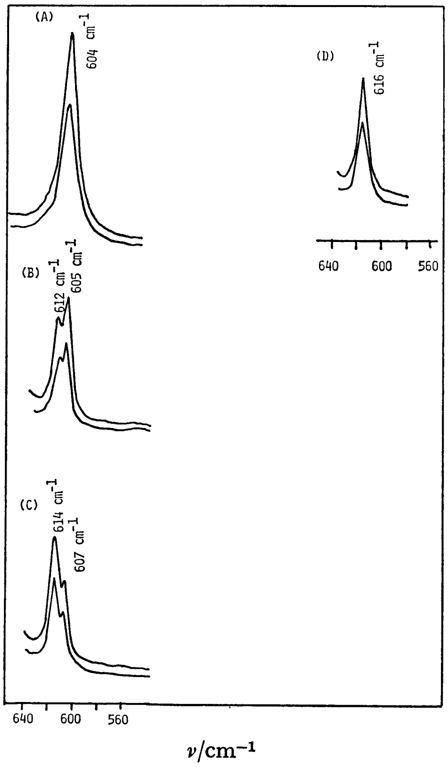

Fig. 3. Raman spectra (560—640 cm^{-1}, $I_{//}$ and $I_{\perp}$) of aqueous solutions of pyridine at room temperature. (A): Pyridine, (B): $X_P=0.746$, (C): $X_P=0.574$, (D): $X_P=0.214$.

same type of spectral change was observed for methanol solutions of pyridine.

(b) Raman Spectral Change with Temperature. Results of measurement are shown in Figs. 4(A), (B), and (C). In the spectrum at 293.0 K in Fig. 4(A), the band at 1576 cm^{-1} is an overlapped band composed of a pyridine band and bands of bonded pyridine as discussed in *(a)*. As temperature falls, the intensity of this band increases greatly, as compared with those of other bands. The band at 1591 cm^{-1} also increases its intensity. However, its degree of change is smaller than that of the band at 1576 cm^{-1}. Moreover, the real increase in intensity of the band of bonded pyridine at 1576 cm^{-1} is far greater than it appears, because the band of nonbonded pyridine overlapping with the bands of bonded pyridine decreases its intensity. Therefore, the band at 1576 cm^{-1} is concerned with a larger enthalpy difference, while the band at 1591 cm^{-1} is concerned with a smaller enthalpy difference. As the band at 1591 cm^{-1} forms a couple with the band at 1585 cm^{-1}, the smaller increase in intensity of the former band relative to the latter band suggests that the couple bands correspond to a species whose enthalpy difference is very small. Thus, the band at 1585 cm^{-1} is not due to only nonbonded pyridine, but to both bonded and nonbonded pyridines. However, it is not the same bonded pyridine that corresponds to the band at 1591 cm^{-1}. For other band couples, as shown in Figs. 4(B) and (C), the bands at 992 and 605 cm^{-1} behave like the one at 1585 cm^{-1}, and those at 998 and 612 cm^{-1} behave as the one at 1591 cm^{-1}. The above results can be interpreted as follows: It is expected that the enthalpy difference for the reaction, pyridine+$CH_3OH \rightarrow \sigma$-complex (one-to-one complex), has a negative value whose absolute value is greater than that of the enthalpy difference for the reaction, σ-complex (one-to-one complex)+$CH_3OH \rightarrow \sigma\pi$-complex. In accordance with this expectation, as shown in Figs. 4(A), (B), and (C), the degree of relative intensity increase of the bands assigned to $\sigma\pi$-complex (1591, 998, and 612 cm^{-1}), compared with their partner bands (1585, 992, and 605 cm^{-1}), is far smaller than that of the band at 1576 cm^{-1} assigned to σ-complexes, $\sigma\pi$-complex, and pyridine. Thus, the band at 1576 cm^{-1} is assigned to nonbonded pyridine, σ-complexes, and $\sigma\pi$-complex, while the band at 1585 cm^{-1} corresponds to nonbonded pyridine and σ-complexes. The band at 1591 cm^{-1} is assigned to $\sigma\pi$-complex. The bands at 992 and 605 cm^{-1} are assigned to nonbonded pyridine and σ-complexes, while those at 998 and 612 cm^{-1} correspond to $\sigma\pi$-complex.

(c) Raman Spectra of Pyridine in Carboxylic Acids. Acetic acid solutions: Though the band of pyridine at 1575 cm^{-1} shifts only by 1 cm^{-1} in aqueous solution, it shifts by 5 cm^{-1} in acetic acid solution. Shift of the band at 1584 cm^{-1} is 16 cm^{-1}, which is larger than that in aqueous solution (10 cm^{-1}). A similar large shift (15 cm^{-1}) is observed for the band of pyridine at 993 cm^{-1}. In acetic acid solution, pyridinium ion coexists with hydrogen bonded pyridines since the bands at 646 and 617 cm^{-1} appearing in the spectrum of the solution correspond to the bands at 642 and 614 cm^{-1} of pyridine dissolved in hydrochloric

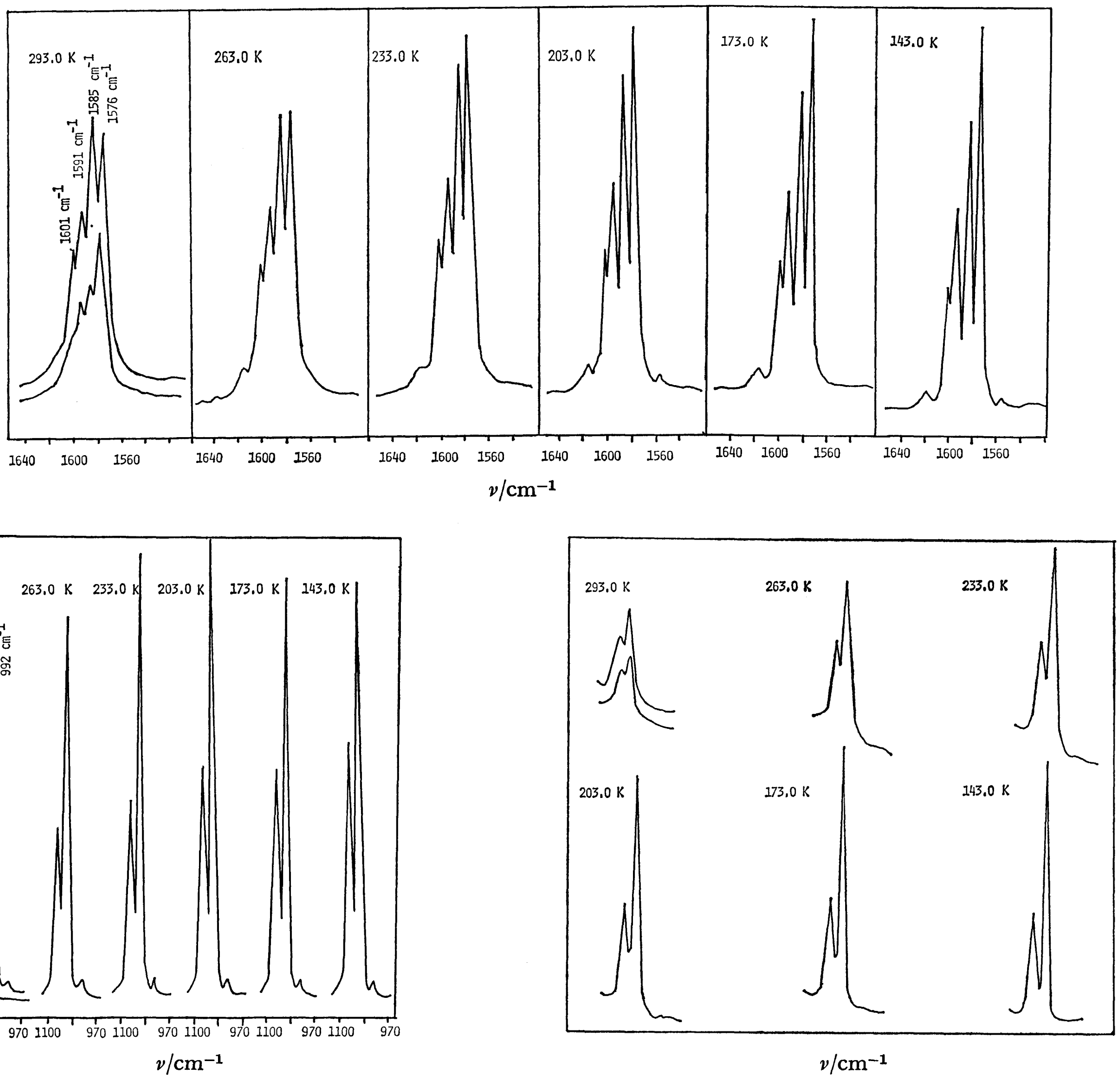

Fig. 4. Raman spectra of a methanol solution of pyridine (a mixture of pyridine and methanol in mol ratio of 1 to 0.526) at various temperatures.
(A): 1540—1640 cm^{-1} region, (B): 970—1100 cm^{-1} region, (C): 580—620 cm^{-1} region.

acid (refer to Table 1 for the solution with a mixing mole ratio of pyridine 1: hydrogen chloride 1.451: water 5.239). Results of measurement are shown in Table 1.

Among the bands of pyridine which shift by hydrogen bond formation, those at 1584, 993, and 605 cm^{-1} are assigned to the C–C ring stretching vibration, the ring breathing vibration, and the CCC and CNC deformation vibration, respectively.[9] As the bonds in the ring are formed primariliy by π-electron bonding, the ring vibrations may be affected by hydrogen bonding to π electrons, and the strength of the bonding may be influenced by the hydrogen bonding power of proton donors. The experimental results in Table 1 show that the shifts of the three bands differ in compliance with the hydrogen bonding power of the two acids. This is consistent with the assignment of the above-mentioned bands to $\sigma\pi$-complex.

(d) Propriety of the Band Assignment. The following calculation suggests that the band assignment discussed in *(a)* and *(b)* above is reliable.

Expressing the peak intensity of a band having frequency f by I_f, we have

$$I_{1576} = I_{1576,\sigma} + I_{1576,\sigma\pi} + I_{1576,\mathrm{P}}, \qquad (1)$$

$$I_{1585} = I_{1585,\sigma} + I_{1585,\mathrm{P}}, \qquad (2)$$

$$I_{992} = I_{992,\sigma} + I_{992,\mathrm{P}}, \qquad (3)$$

$$I_{998} = I_{998,\sigma\pi}, \qquad (4)$$

where σ, $\sigma\pi$, and P denote σ-complexes, $\sigma\pi$-complex, and pyridine, respectively. Denoting the ratio $I^{\circ}_{1575}/I^{\circ}_{1585}$ for pure pyridine by r and assuming that $I_{1576,\sigma}+I_{1576,\mathrm{P}}=(I_{1585,\sigma}+I_{1585,\mathrm{P}})r$, the quantity $r_{\sigma\pi}$, proportional to the mole fraction of $\sigma\pi$-complex, will be obtained from Eqs. 1 and 2 for the solution corresponding to Fig. 1(B):

$$r_{\sigma\pi} = (I_{1576}-I_{1585}r)/I_{1576} = 0.38,$$

for which the observed value of r=0.638 is used. On the other hand, $r_{\sigma\pi}$ can be obtained by Eqs. 3 and 4 for the same solution as

$$r_{\sigma\pi} = I_{998}/(I_{998}+I_{993}) = 0.36.$$

Table 1. Raman shift frequencies of pyridine in acids and pyridinium ion (in cm^{-1})[a]

Pyridine	CH_3COOH soln[b]	HCOOH soln[c]	Pyridinium ion
379 (0)	385 (0)	385 (1)	
	403 (1)	407 (2)	400 (2)
409 (1)	414 (1)	415 (2)	
	610 (sh, ?)	608 (2)	614 (6)
605 (1)	617 (2)	627 (2)	
	645 (sh, ?)	642 (sh, ?)	642 (8)
655 (4)	655 (10)	655 (13)	
980 (4)	983 (4)	983 (6)	
993 (100)	1008 (100)	1012 (100)	
	1011 (sh, ?)		1011 (100)
	1035 (sh, ?)		1029 (35)
1031 (75)	1038 (28)	1035 (81)	
	1065 (sh, ?)	1063 (sh, ?)	1063 (6)
1072 (1)	1070 (2)	1068 (3)	
1148 (1)	1154 (1)	1156 (1)	
	1204 (sh, ?)	1204 (sh, ?)	1204 (4)
1218 (3)	1217 (5)	1220 (8)	
	1240 (1)	1247 (sh, ?)	1247 (1)
	1260 (1)	1260 (1)	1258 (1)
1485 (1)	1489 (1)	1490 (2)	
1575 (2)	1580 (2)	1580 (sh, ?)	
1584 (3)	1600 (2)	1603 (3)	
	1625 (1)	1625 (1)	1625 (1)
1602 (1)	1631 (1)	1638 (1)	
	1644 (1)	1644 (sh, ?)	1644 (3)

a) Figures in parentheses represent relative intensity. b) Mixture of pyridine and acetic acid in a mole ratio of 1 to 1.487 (pH=4.17). c) Mixture of pyridine and formic acid in a mole ratio of 1 to 1.519 (pH=3.65).

In the same way, $r_{\sigma\pi}$ for the solution corresponding to Fig. 1(C) is obtained as 0.60 and 0.58 from Eqs. 1 and 2 and from Eqs. 3 and 4, respectively. This good agreement of the $r_{\sigma\pi}$ values from the two sets of equations suggests a reliability of the assignment of the band at 1576 cm^{-1} to σ-complexes, σπ-complexes, and pyridine, and those at 1585, 993, and 606 cm^{-1} to σ-complexes and pyridine, and those at 1591, 998, and 616 cm^{-1} to σπ-complex.

(e) Quantitative Relation between the Relative Intensities of the Bands at 992 and 998 cm^{-1} and Temperatures. As shown in Fig. 5, an almost linear relation holds between $\ln(I_{992}/I_{998})$ and $(1/T)$. Although equilibria in the solution are not known, this result suggests that (I_{992}/I_{998}) is approximately proportional to an equilibrium constant. The quantity ΔH obtained from the straight line in the figure on the basis of the equation

$$\ln(I_{992}/I_{998}) = -\frac{\Delta H}{RT} + \text{const.}$$

may be related to the enthalpy difference for the reaction concerning the equilibrium constant. The value for the ΔH is 0.9 ± 0.2 kJ mol^{-1}, whose absolute value is very small compared with those of enthalpy differences for ordinary σ-type hydrogen bonds. Therefore, the equilibrium which predominates the temperature change in (I_{992}/I_{998}) might be the equilibrium between σπ-complex and σ-complexes.

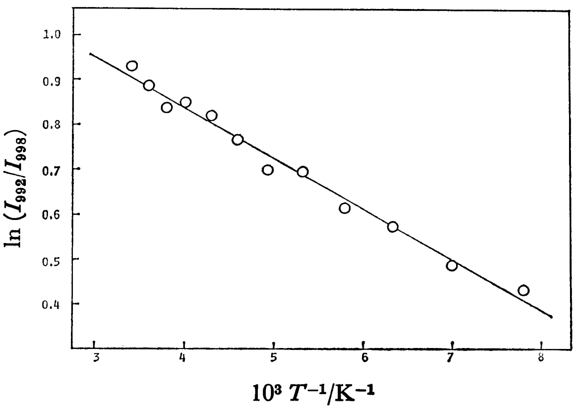

Fig. 5. Relation between $\ln(I_{992}/I_{998})$ and $(1/T)$. T in K.

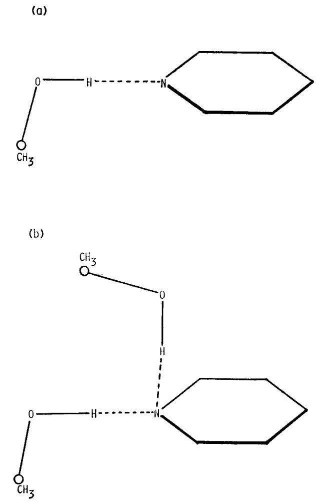

Fig. 6. σ-Complex (a) and σπ-complex (b).

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