Intermolecular Hydrogen Bonds and Orientational Correlation Times of Monomers and Associates in Pyridine Solutions

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In Raman spectra, the 992 cm^{-1} band of pyridine under its dilution in a proton donor solvent is split into two bands: a 992 cm^{-1} monomer band and an ~ 1000 cm^{-1} aggregate band; the aggregate band has a complicated shape. The change of the pyridine and iso-propyl alcohol composition in binary solvents allows us to establish the presence of two lines with wave numbers 998.5 and 1001 cm^{-1} in the aggregate band, which are associated with simple and complicated aggregates. The band depolarization ratios were determined, and were found to be different; the widths of the isotropic and anisotropic components of the band were also determined. Calculations using the anisotropic component band widths allow us to determine (approximately) the relaxation times of the orientational correlation of monomers, and of the simple and complicated aggregates of pyridine in the mixture. For solutions of pyridine-iso-propyl alcohol, these times were found to be 4.1, 11.0, and 21 ps, respectively.

The dilution of pyridine–isopropyl alcohol by heptane allows us to improve the resolution of the bands. As a result, the half widths of the isotropic components of the bands were obtained, and the vibrational relaxation times for pyridine were calculated, for which all types of aggregates were found to differ only slightly.