

Structure of polarized Raman scattering lines in ternary mixture

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The narrowing of polarized lines in the Raman spectrum which has been found experimentally to accompany the dilution of a substance in a neutral solvent has been utilized to resolve the structure of a line ($\sim 1000\text{ cm}^{-1}$) of pyridine groupings in a mixture with butyl alcohol and heptane. The same method has been used to resolve the structure of the 992-cm^{-1} line of a pyridine-chloroform-heptane mixture.

The width of polarized components of Raman scattering lines is in several cases very sensitive to a dilution of the substance with a neutral solvent.¹ The usual effect is a decrease in linewidth: The vibrational relaxation time increases. For example, in our experiments in which benzene or pyridine was diluted with a neutral solvent, heptane, the width of the polarized line at 992 cm^{-1} decreased by a factor of 2.5 (Refs. 2 and 3). In an extremely dilute solution (with a molecular ratio 1:50) of either pyridine or benzene with heptane, the width of this line is 1 cm^{-1} . This circumstance might be utilized to improve the resolution of closely spaced polarized Raman lines which cannot be resolved in the pure liquid because of a large half-width. In fact, for a given spectral apparatus, the resolution of spectral lines depends on the half-width of the lines and on the characteristics of the apparatus.

As the linewidth decreases, the resolution should improve. We have used this method to resolve the structure of the line at $\sim 1000\text{ cm}^{-1}$ of pyridine groupings with butyl alcohol. The spectra were recorded on a DFS-52 spectrometer. An intermolecular hydrogen bond is known to form between the molecules of the components of this mixture.⁴ In a binary mixture one observes, in addition to the line of monomer molecules at 992 cm^{-1} , a line of groupings with a wave number $\sim 1000\text{ cm}^{-1}$. As the butyl alcohol content is increased in a binary mixture, the intensity of the line of the groupings increases, as has been established previously. In addition, the line broadens, goes through a maximum width, and then narrows with a further dilution. These events are accompanied by a shift of the peak of this line, of 2.5 cm^{-1} in the direction of higher frequencies.

In an effort to determine the structure of this line, we used a method involving a ternary mixture: We diluted a mixture of pyridine and butyl alcohol with heptane. The results of these experiments are shown in Fig. 1. We see that the polarized lines of both the monomers (992 cm^{-1}) and the groupings ($\sim 1000\text{ cm}^{-1}$) have become markedly narrower. As a result, we see a doublet structure in the line of the groupings. The intensity ratio of the components of the doublet varies with the butyl alcohol content. We believe that the line at 998.5 cm^{-1} corresponds to 1:1 pyridine-(butyl alcohol)

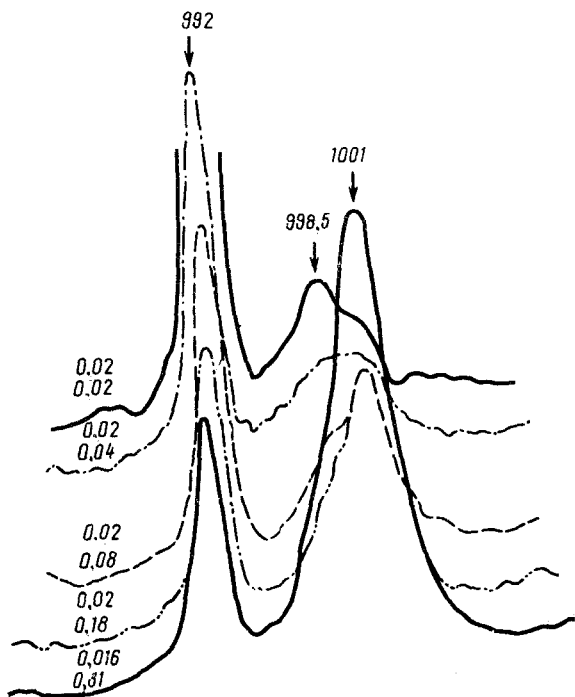


FIG. 1. Structure of the line at 992 cm^{-1} of pyridine in a mixture with butyl alcohol and heptane (the heptane concentration ranged up to 1 mf).

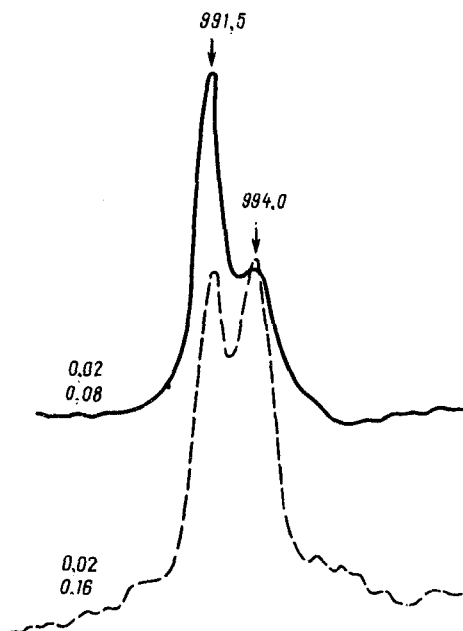


FIG. 2. The line at 992 cm^{-1} of pyridine in a ternary pyridine- CHCl_3 -heptane mixture (the heptane concentration ranged up to 1 mf).

groupings, while the line at 1001 cm^{-1} corresponds to more complex groupings. The ternary-mixture method has also made it possible for us to resolve the structure of the line at 1030 cm^{-1} of pyridine in a mixture with butyl alcohol and heptane. This line also turns out to be a doublet.

The method described above has also made it possible for us to determine the proton-donating capability of chloroform molecules in a mixture with pyridine.⁵ In a binary chloroform-pyridine mixture, the only noticeable effects are a broadening of the line at 992 cm^{-1} and a shift of this line up the frequency scale. In a ternary mixture, it is possible to resolve the structure of this line (Fig. 2): It turns out to be a doublet. With increasing content of the active components, there is a redistribution of intensity between the lines of this doublet in the manner characteristic of the formation of a hydrogen bond.

¹A. A. Rodiriguos and M. Schwartz, *Spectrochim. Acta* **44**, 43 (1988).

²F. H. Tukhvatullin *et al.*, in *Seventh Annual EMLG Conference "Statistical Mechanics of Chemically Reacting Liquids."*

³A. K. Atakhodjaev *et al.*, in *Twenty-sixth CSI Symposium*, Sofia, 1989, p. 4.

⁴I. Bradmüller and G. Mozer, *Introduction to Raman Spectroscopy* [Russian translation], Mir, Moscow, 1964, p. 628.

⁵G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, Freeman, San Francisco, 1960.

Translated by Dave Parsons