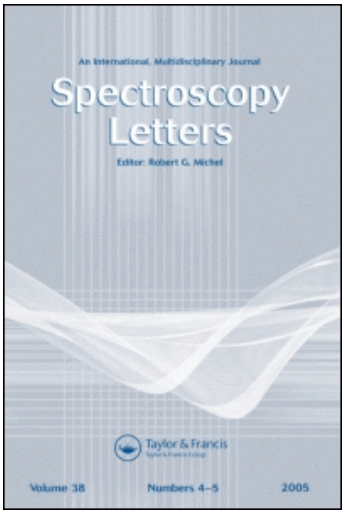

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Effect of Some Aromatic Admixtures on the Raman Line Intensity of Solid Cyclohexane at 77 K

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EFFECT OF SOME AROMATIC ADMIXTURES ON THE RAMAN LINE INTENSITY OF SOLID CYCLOHEXANE AT 77 K

Key words: Raman spectroscopy, admixture in cyclohexane

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ABSTRACT: The dependence of the intensity of Raman line components of E_g symmetry of cyclohexane, frozen rapidly down to 77 K, on the concentration of admixtures of benzene or naphtalene was studied quantitatively. The admixture of benzene was found to facilitate to a larger extent the overcooling of phase I of solid cyclohexane than admixture of naphtalene.

Frozen cyclohexane has two stable crystal phases: high-temperature (I) and low-temperature (II) with a phase transition at 186,1 K, as well as a third one (III), which is methastable between 120 K and 77 K; both the stable phases I and II have been intensively studied spectroscopically and crystalographically, but the metastable phase III is almost unknown /1-3/. When pure cyclohexane is rapidly cooled down to 77 K, a policrystaline mixture of phase II and overcooled phase I is obtained and the mixture is assumed to contain also overcooled

phase III /3, 4/. The rapid overcooling of phase I of solid cyclohexane has been observed to occure more easily with increasing amount of admixtures in a Raman study /4/ for assumed aliphatic impurities and in an ultraviolet study /5/ for benzene admixtures. Unfortunately, the results given in these studies are qualitative only.

The results from a quantitative study of effect of some aromatic admixtures on the overcooling of phase I for cyclohexane, rapidly cooled to 77 K, are given in this paper.

In our experiments, samples of spectroscopically pure cyclohexane with added admixtures of benzen or of naphtalene in the 1×10^{-1} - 1×10^{-5} mol. l^{-1} range were placed in a cell and rapidly cooled for about 2 minutes to 77 K by placing the cell directly in liquid nitrogen. The Raman spectra of the samples were obtained by using an optical cryostat, a 30 mW cadmium laser (441, 6 nm wave length) and a three-prismes spectrograph. For each admixture concentration two 2-hour exposures on photoplate were made.

We have chosen for our purposes to study the intensities of two Raman fundamentals ν_{20} and ν_{19} of solid cyclohexane; these fundamentals are of E_g symmetry and they were proved to split into two components only /6, 4/. In our spectra these two fundamentals have slightly overlapping components at 1342 cm^{-1} and 1348 cm^{-1} or 1441 cm^{-1} and 1448 cm^{-1}, respectively. The low-frequency component, which is less intense, corresponds always to phase II, whereas the high-frequency component is due to overlapping of the experimentally indistinguishable components of phase I and phase II /4/. The fundamental ν_4 of solid cyclohexane was chosen as reference for the studied line intensities. This fundamental is of A_{1g} symmetry, it is not split into components and thus it is not affected by the varying phase ratio in solid cyclohexane /6, 4/. This vibration ν_4 was recorded in our spectra at 1161cm^{-1}.

The blackening along the profile of the studied Raman lines ν_{20} and ν_{19} was recorded using a microdensitometer by scanning at three different places of the spectrum height and subsequently averaging the results. When using the blackening curve of the photoplate, the line profile was plotted from the average values in terms of their intensity. different places of the spectrum height and subsequently averaging the results. When using the blackening curve of the photoplate, the line pro-

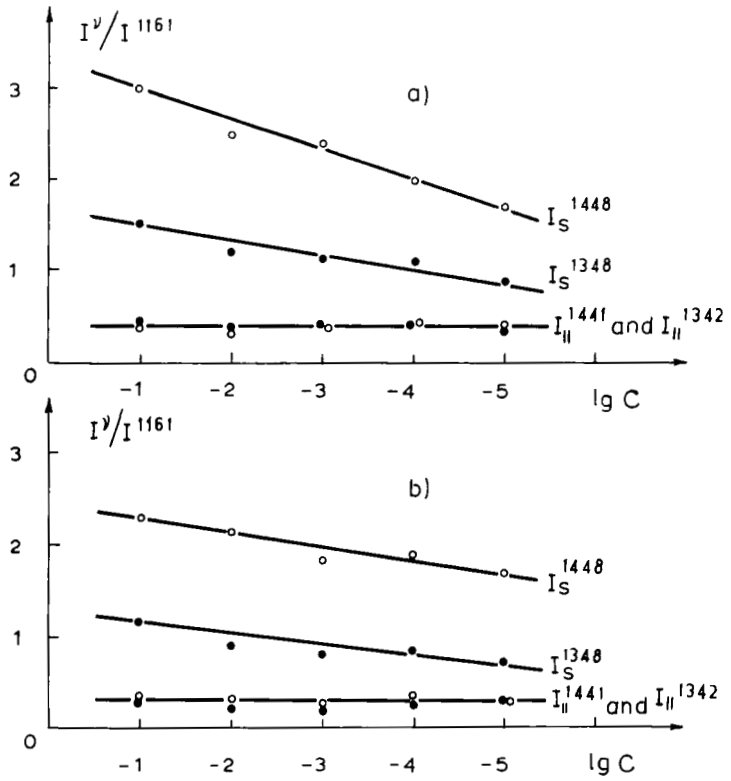

Fig. 1

Dependence of the relative intensities I_{II}^{1342}, I_s^{1348}, I_{II}^{1441} and I_s^{1448} of the ν_{20} and ν_{19} Raman line components of solid cyclohexane at 77 K on the molar concentration c of admixtures of benzene (Fig. 1-a) and naphtalene (Fig. 1-b). The notations are: ● for I_{II}^{1342} and I_s^{1348} : o for I_{II}^{1441} and I_s^{1448}.

file was plotted from the average values in terms of their intensity. This profile is graphically decomposed into the two components mentioned above and their maximum intensity are read out: I_{II} for the low-frequency component corresponding to phase II only and I_s for the high-frequency component corresponding to the sum of components of phase I and II. In this procedure we consider that under the existing conditions, there is no contribution to I_s intensity by the metastable phase III. Finally we take the

ratio of each of the intensities thus obtained I_{II} and I_s to the maximum intensity I of the reference 1161 cm^{-1} Raman line, found in similar way. The result from all determinations shown in Fig. 1 is obtained from data which are mean values for the two exposures of each sample.

It is seen from the plots in Figures 1-a and 1-b that the phase II low-frequency component intensity I_{II} for the two fundamentals ν_{20} and ν_{19} is not affected by the admixture concentration. On this basis we may assume that the intensity of the high-frequency component of phase II giving a contribution to the intensity I_s shows the same dependence on the admixture concentration. Consequently, the clearly expressed enhancement of the intensity I_s with increasing benzene or naphtalene admixture concentration may be due only to an increased contribution of the component which corresponds to the overcooled phase I of solid cyclohexane.

It may be calculated from the plots in Fig. 1 that when the admixture concentration is increased from 1×10^{-5} to 1×10^{-1} $mol.l^{-1}$, the relative contribution of phase I to the intensity I_s increases on the average by about 50% for naphtalene and about 70% for benzene. We have thus found that admixtures of benzene facilitate to a certain extent more strongly the overcooling of phase I of cyclohexane rapidly cooled to 77 K, than admixtures of naphtalene. The absolute amount of the two stable phases I and II of solid cyclohexane cannot be assessed quantitatively.

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