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Note on Raman Spectra of Para-Azoxydianisole in CCl_4

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Abstract The Raman spectra of p-azoxydianisole(PAA) were observed in the solid phase and its carbon tetrachloride solution for a spectral range of 1100–1600 cm^{-1} . Differences in the frequencies at the peaks of spectral bands and in the band shape between the corresponding bands were clearly observed.

Introduction

Recently, many investigations of the intermolecular interaction in liquid crystals have been carried out using Raman scattering technique¹⁻³⁾. Especially, the effects of the phase transitions on Raman spectra of such compounds have been discussed in detail.

In 1972, Raman spectra of four 4,4'-bis(alkoxy) azoxy-benzenes in the solid, nematic and liquid phases were investigated by Amer and Shen¹⁾. But, in order to make clear the intermolecular interaction with use of vibrational Raman spectra, some information on the isolated molecules will be necessary.

In this paper, Raman spectrum of p-azoxydianisole(PAA) dissolved in carbon tetrachloride is compared with that of pure PAA in solid phase. Raman spectrum of PAA in carbon tetrachloride is considered as that of isolated PAA molecules. Therefore, such a comparison will be available for determination of the nature of the intermolecular interaction in nematic compounds.

Experimental

An Echell grating monochromator and a photon counting system with a cooled photomultiplier (HTV-R376) were employed in the present measurement.

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The slit widths were 2.0 cm^{-1} for pure PAA and 2.7 cm^{-1} for PAA in carbon tetrachloride. The vibrational frequencies were calibrated using the emission lines of Hg, Cd and Na lamps and the known Raman lines of CCl_4 , C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$. Frequencies were estimated to be correct to $\pm 1.5\text{ cm}^{-1}$. The intensities were calibrated for pre-slit optical system, monochromator and detector with use of the standard lamp of Toshiba. The intensities had an accuracy within $\pm 20\%$.

The exciting sources were a He-Ne laser operated at 6328 \AA and a He-Cd laser at 4416 \AA . The former was used for the solid PAA and the latter for PAA in carbon tetrachloride.

The sample of pure PAA was contained in 1mm-diameter capillary tube which was kept at $69.8^\circ\text{C} \pm 0.1^\circ\text{C}$. The mole ratio of PAA in carbon tetrachloride was 0.005 and its spectrum was observed at room temperature.

Results

For a spectral range of $1100\text{--}1600\text{ cm}^{-1}$, Raman spectra of solid PAA and PAA dissolved in carbon tetrachloride were observed. The traces of these spectra are shown in Figures 1 and 2. The spectrum of solid PAA was nearly the same as that observed by Amer and Shen¹⁾, but the peak position of the 1501 cm^{-1} band in their paper was observed at 1494 cm^{-1} in our measurement and their 1582 cm^{-1} band could not be observed because of the appearance of the emission line of neon in this neighborhood.

Comparing Raman spectrum in solid PAA with that of PAA- CCl_4 solution, we note the following facts:

1. For the bands at 1114 , 1172 , and 1571 cm^{-1} , any differences in the positions of the band peaks or in the band shapes were not found between two spectra.
2. For the bands at 1095 , 1157 , 1319 , 1332 , 1410 , 1494 , and 1598 cm^{-1} , the frequencies of band peaks in PAA- CCl_4 solution were larger than those of the corresponding bands

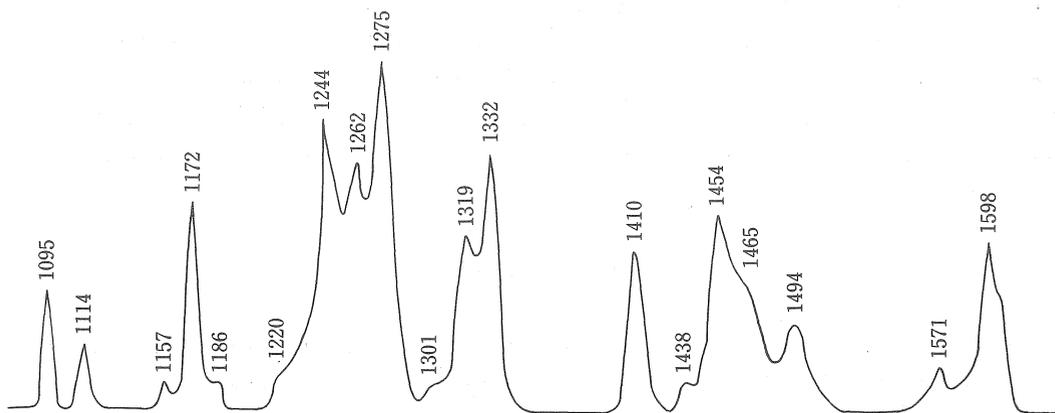


Fig.1. Raman spectrum of PAA in the solid phase at 69.8°C

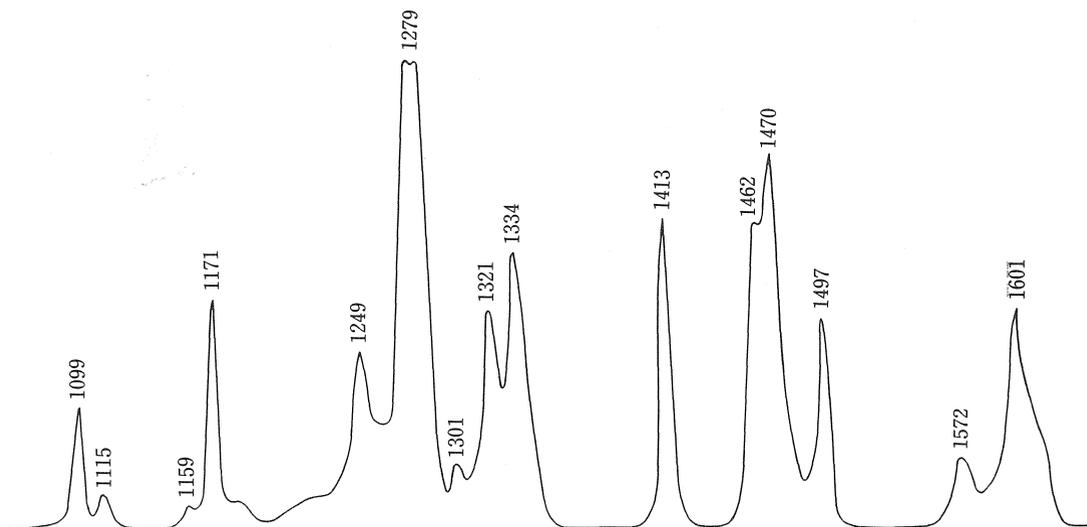


Fig.2. Raman spectrum of PAA in carbon tetrachloride solution, mole ratio of PAA : 0.005

in solid PAA by $2\sim 4\text{ cm}^{-1}$. But the band shapes were not different between two spectra.

3. For the bands in the regions of $1244\text{--}1275\text{ cm}^{-1}$ and $1438\text{--}1465\text{ cm}^{-1}$, the band contours were essentially different between two spectra. The band shape of PAA in solution in the region of $1244\text{--}1275\text{ cm}^{-1}$ is similar to that observed by Amer and Shen in the nematic and liquid phases of PAA¹⁾, but its peak frequencies were different from their values. On the other hand, the band shape of PAA in solution in $1438\text{--}1465\text{ cm}^{-1}$ was different from that observed by Amer and Shen in the nematic and liquid phases of PAA.
4. The intensities of the bands at 1114 , 1410 , and 1494 cm^{-1} relative to 1095 cm^{-1} band in PAA- CCl_4 solution were about twice as large as those of corresponding bands in solid PAA.
5. For the bands at 1186 , 1220 , and 1301 cm^{-1} , the comparison was impossible because of weak intensity,

Bulkin et al. concluded⁴⁾ that the infrared spectra of solutions of PAA in CCl_4 and CS_2 were virtually the same as those of the isotropic liquid PAA. However, in our results of Raman scattering, fairly large changes were observed in both the frequency of band peak and band shape. In this respect, further study will be necessary.

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