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Raman Spectroscopy Studies of Reorientations in Isotropic Phase of Alkoxyazoxybenzenes†

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Raman spectra for isotropic phase of PAA, PAP and HOAB were recorded. Three benzene rings vibrations were chosen for quantitative analysis and the choice is discussed for different PAA deuteration. The separation of vibrational and rotational relaxation was performed. Vibrational relaxation is a dominating process, but ca. 10% of total bandshape can be attributed to rotational relaxation. Rotational correlation times τ_2 were calculated for all studied substances to be of the order 10^{-11} s. τ_2 is connected with the rotation around the long molecular axis and supports the correlation time τ_1 received from the dielectric relaxation measurements.

I. INTRODUCTION

A few years ago Lugomer[1] published a paper dealing with IR spectroscopic investigations of fast rotational motions of liquid crystals. Based upon those results, he then calculated correlation functions and correlation times for the rotation around the long molecular axis of the order 10^{-12} s for diheptyloxyazoxybenzene (HOAB). He assumed the rotational relaxation to be the dominating process of band broadening and, hence, other processes could be neglected. Results of following such a procedure seem doubtful, because the studies performed for isotropic liquids led to the conclusion that vibrational relaxation was dominating and should not have been neglected.[2] In addition, the dielectric relaxation studies performed for HOAB gave

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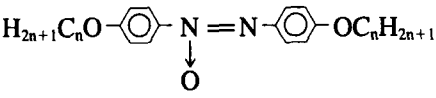
the relaxation time of the order 10^{-11} s, for both the nematic and the isotropic phase.[3]

There are other results for vibrational relaxation, using Raman spectroscopy in other liquid crystal molecules (cyano biphenyl derivative) where rotational relaxation is neglected.[4]

Therefore, we have decided to carry out studies of several well known liquid crystals of alkoxyazoxy-benzenes homologous



series, namely p-azoxyanisole (PAA, n = 1), p-azoxyphenetole (PAP, n = 2) and di-heptyloxyazoxybenzene (HOAB, n = 7). The aim of my study was to check which of those processes actually dominates in molecules of liquid crystals. For normal liquids the Raman spectroscopy is a very powerful technique that permits a study of fast molecular relaxations (10^{-11} – 10^{-12} s correlation times) so it was applied. To avoid the problem of the proper value of order parameter and mono- or polycrystallinity and surface alignment the isotropic phase of liquid crystals was examined.

Preliminary results for PAA and HOAB have already been published[5] and this paper presents a more detailed analysis of those results. In addition, the results for PAP are reported and the choice of the band for quantitative analysis is discussed. The conclusions concerning both the advantages and the limitations of this method are drawn.

II. EXPERIMENTAL PROCEDURE

The experiments for PAA and HOAB were carried out with Varian Cary 82 Raman spectrometer (with triple monochromator). Argon laser (from "Spectra Physics") green line 5145 Å excitation line was used. The sample was placed in a glass cylindrical container with the diameter of ca. 8 mm, heated by means of direct contact with the heating metal element. The thermocouple controlling the temperature was placed on the surface of the container on the opposite side of the heater. The vertically polarized incident beam was scattered by the isotropic sample and the scattered light was collected at the angle of 90°, after passing through the polarizer, placed parallel or perpendicular to the incident beam polarization. As a result, two spectra were recorded: VV for parallel and VH for perpendicular polarizer positions.

The experiments for PAP were performed with the use of a Spex Ramalog 14018 spectrometer with double monochromator (1800 lines/mm holo-

graphic gratings). The 5145 Å green line of the "Spectra Physics" argon laser excitation line was used. The sample was placed between glass plates. The Mettler FP 52 hot stage was used as heater with the FP 5 controller for temperature control. The scattered light was collected at the angle of 180° ("back-scattering" technique). The polarizer was placed in front of the entrance slit of the monochromators. The VV and VH spectra were recorded by the photon counting system.

In all the measurements, the temperature was fixed, ca. 5°C above the clearing point of the sample. The substances were spectroscopically pure (PAA and HOAB from E. Merck, PAP was synthesized in cooperating organic laboratory of Agro-Pedagogical University in Siedlce). The spectra for the chosen bands were recorded many times with very good resolution (slitwidth $\leqslant 1$ cm^{-1}) and with high sensitivity. The power of the incident laser beam on the sample was usually ~ 100 mW.

In the experiments with partially deuterated PAA samples the spectra for polycrystalline powder in room temperature were recorded using the Cary 82 spectrometer. The substance was pressed into a tiny hole of a steel needle placed at 45° to the incident laser beam.

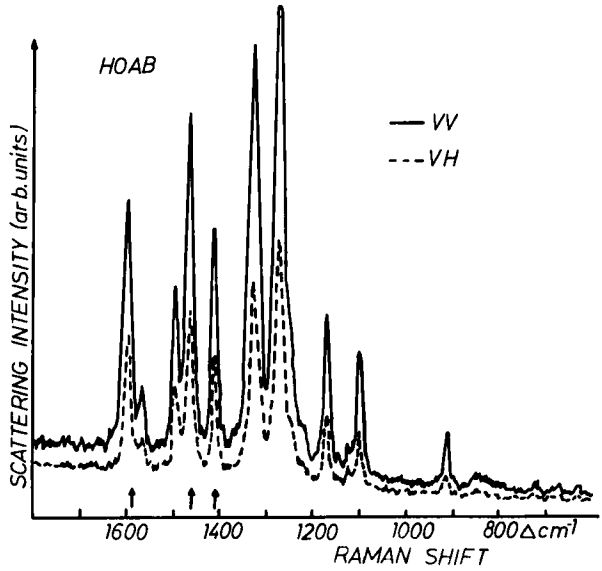


FIGURE 1 Raman spectrum for isotropic phase of HOAB. Solid line corresponds to VV geometry, broken line–VH geometry. Arrows mark the bands chosen for further analysis.

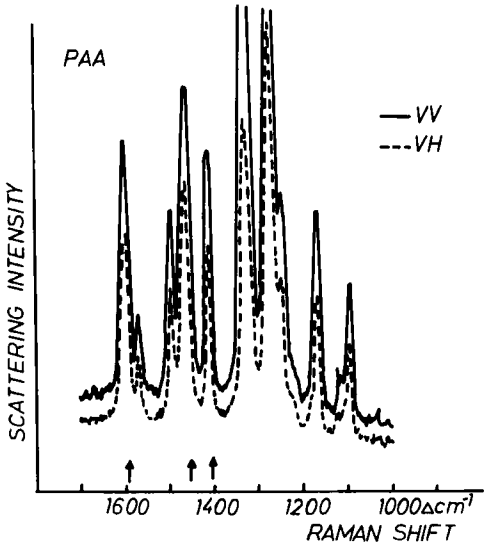


FIGURE 2 Raman spectrum of isotropic phase of PAA.

III. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectrum for isotropic phase of HOAB in the range 600–1800 cm^{-1} for VV and VH geometry. This result is in agreement with those formerly published by Amer and Shen.[6] As shown in Figure 2 the PAA spectrum in this range is very similar to that in Figure 1. Arrows mark the bands chosen for quantitative analysis. The bands are assigned to be connected with deformational vibrations of benzene rings. They appear at almost the same frequencies (ca. 1410, 1460, 1600 cm^{-1}) for all alkoxyazoxybenzenes measured. Moreover, to prove this assignment experimentally the measurements were performed with partially deuterated PAA to compare the spectra of 3 "substances" PAA d_o — no deuterium, PAA d_6 deuterated terminal methyl groups and PAA-d_8 — deuterated phenyl rings.

The results are shown in Figure 3. The bands for PAA d_0 and PAA d_6 appear at the above mentioned frequencies in this range of spectrum. However, the spectrum for PAA-d_8 in this range is shifted toward lower frequencies. Therefore, selecting just these three bands marked in Figures 1 and 2 for further studies seems reasonable. It should be pointed out that the whole molecule is involved in each vibration and the assignment of the band to the vibration of a part of the molecule is an approximation only. It is generally accepted, because it is supported by the potential energy distribution calculations,[7] that there are bands where the vibrations of part of molecule dominate.

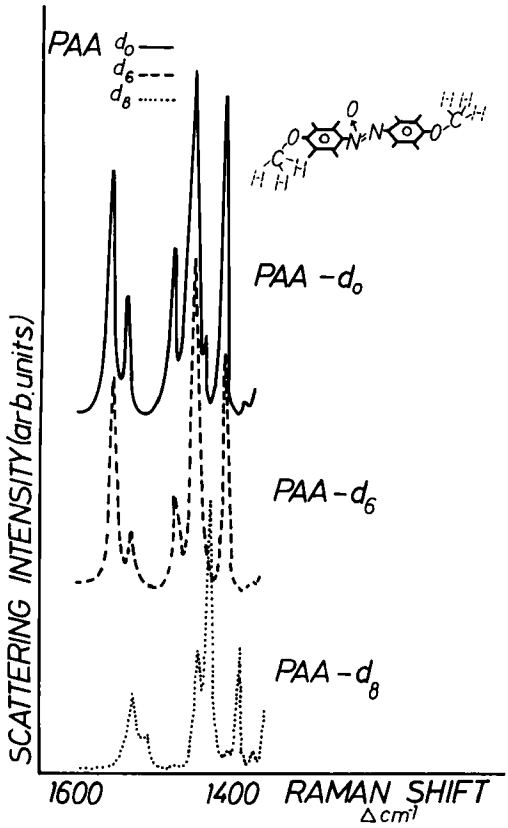


FIGURE 3 Comparison of Raman spectrum of PAA-d_0 (solid line), PAA-d_6 (broken line) and PAA-d_8 (dotted line).

The bands chosen for studies of the bandshape were recorded many times with good resolution (spectral slitwidth $\leqslant 1$ cm^{-1}), that in turn required very high sensitivity of photomultiplier tube. Thus, the influence of the slitwidth on the bandshape could be neglected. The Raman spectrum in the range 1400–1500 cm^{-1} for PAP is shown in Figure 4 as an example.

An analysis of the bandshape was made by separating the vibrational and rotational processes developed for pure isotropic liquids by Bartoli-Litovitz[8] and Nafie-Peticolas.[9] The main assumption here is the independence of those two processes. The vibrational and rotational parts of the band are connected with isotropic and anisotropic parts of the polarizability tensor of a molecule. Its isotropic part results from vibrational relaxation and the difference between anisotropic and isotropic parts is connected with rotation. Thus

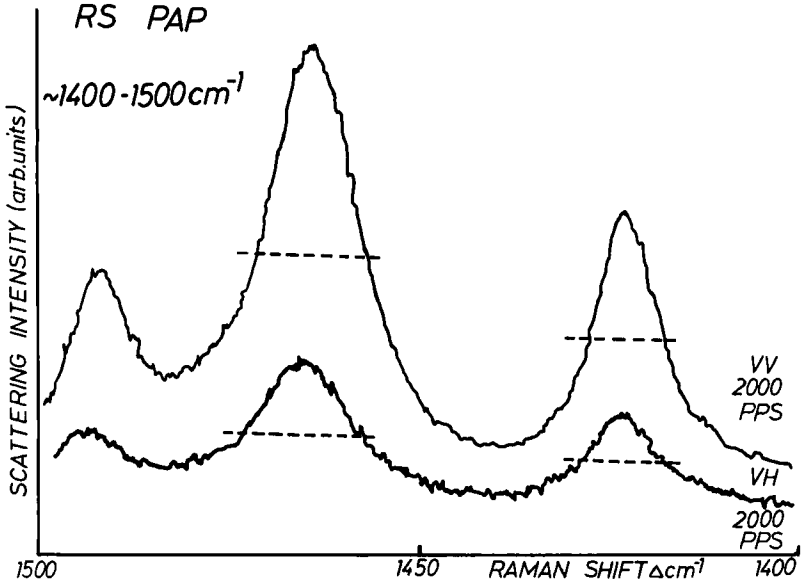


FIGURE 4 Raman spectrum of PAP in isotropic phase in the range 1400–1500 cm^{-1} (upper curve for VV, lower–VH geometry).

$$I_{VH}(\omega) = I_{\text{aniso}}(\omega) \tag{1}$$

$$I_{VV}(\omega) = I_{\text{iso}}(\omega) + \frac{4}{3} I_{\text{aniso}}(\omega), \tag{2}$$

where I–intensity, ω–frequency, VV, VH–experimental geometry.

For the Lorentzian bandshapes

$$\Gamma_{\text{iso}} = \Gamma_{\text{vib}} \tag{3}$$

$$\Gamma_{\text{aniso}} - \Gamma_{\text{iso}} = \Gamma_{\text{rot}}, \tag{4}$$

where Γ states for full width at half maximum of intensity. From Γ_{rot} rotational correlation time τ_2 can be calculated

$$\tau_2 = (\pi c \Gamma_{\text{rot}})^{-1} \tag{5}$$

Equation 5 can be also used to calculate vibrational correlation time τ_{vib} placing τ_{vib} instead Γ_{rot}.

The results of experimental data processed in this way are shown in Tables I and II. The results presented in Table I by the very small deviations of depolarization ratios and vibrational halfwidth prove good reproducibility of the measured spectra. Vibrational halfwidth and vibrational

TABLE I

Depolarization ratios and vibrational relaxation data for isotropic phase of alkoxyazoxy-benzenes

	ν_{max} [cm^{-1}]	ρ	Γ_{vib} [cm^{-1}]	τ_{vib} [10^{-12} s]
PAA	1409	0.32 ± 0.01	9.8 ± 0.4	1.1
	1458	0.33 ± 0.02	21.8 ± 0.3	0.5
	1596	0.38 ± 0.01	17.1 ± 0.5	0.6
PAP	1405	0.36 ± 0.08	11.0 ± 0.8	1.0
	1450	0.33 ± 0.05	16.4 ± 0.4	0.6
	1590	0.38 ± 0.01	19.2 ± 0.5	0.5
HOAB	1408	0.33 ± 0.02	9.4 ± 1.1	1.1
	1460	0.33 ± 0.02	17.0 ± 1.0	0.6
	1592	0.37 ± 0.01	18.0 ± 1.1	0.6

TABLE II

Rotational relaxation data for isotropic phase of alkoxyazoxy-benzenes

	No. of measurements	Γ_{rot} [cm^{-1}]	τ_2 [10^{-12}]
PAA	17	0.8 ± 0.4	12
PAP	11	1.3 ± 0.7	8
HOAB	20	1.0 ± 0.5	10

relaxation time are characteristic for every vibration. For solutions they depend on solvent and temperature, but in pure liquids depend on temperature only and this dependence is usually small. On the other hand, the rotational relaxation corresponding to molecular reorientations around its long axis has one value independent of the band chosen for analysis (the reorientations can be observable, or $\Gamma_{rot} = 0$). Therefore, in Table II there is only one Γ_{rot} for each substance. The comparison fo Γ_{rot} and Γ_{vib} from Table I and II clearly shows that the vibrational relaxation dominates in each case studied and, therefore, cannot be neglected. But the rotational part of the bandshape is also significant and cannot be omitted in any detailed analysis.

The rotational correlation times obtained here are in agreement with those given in [3,10] calculated from dielectric relaxation studies.

CONCLUSION

The present investigation shows that the vibrational relaxation dominates in the bandshape and therefore cannot be neglected in any spectroscopic

study. Its correlation time for band studied here is $10^{-13} - 10^{-12}$s. The rotational relaxation part of the bandshape for alkoxyazoxybenzenes is small (ca. 10%) but still significant.

Rotational correlation times for reorientations around long molecular axis for three studied substances (PAA, PAP and HOAB) are of the order 10^{-11}s and in agreement with dielectric relaxation studies.

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