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RAMAN SPECTRA OF ALIGNED THIN FILMS OF NEMATIC LIQUID CRYSTAL (MBBA)

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The Raman spectra of thin films of a nematic liquid crystal, p-methoxybenzylidene-p'-n-butylaniline (MBBA), have been measured for the samples aligned on glass (or quartz) surface homogeneously and homeotropically, respectively. The results confirm the molecular arrangements suggested by the observation with a polarizing microscope. The intensity changes and polarization components of the Raman bands are useful for the vibrational assignments.

Molecular orientation in nematic liquid crystals is usually suggested by observation with a polarizing microscope.[1,2] It has, however, not always been clarified in molecular dimension, because X-ray studies of nematic phase usually yield no precise information regarding the arrangement of the molecules.[3] It is desirable to get more definite information of the molecular orientation of liquid crystals at the glass (or quartz) surfaces of different natures due to previous treatment. Since laser Raman spectroscopy is now available for the clarification of surface structures,[4,5] Raman spectra of thin films of a nematic liquid crystal, MBBA, have been studied for the samples supposed to have homogeneous and homeotropic alignments.

Guaranteed reagent of p-methoxybenzylidene-p'-n-butylaniline (MBBA) was obtained from Tokyo Chemical Co. and was used without further purification. Windows, glass or quartz plates (optically flat and 25 x 75 x 1 mm large), were cleaned by use of a chromic acid cleaning solution.

For obtaining homogeneous alignment, the clean window surfaces were rubbed with a silk cloth in the direction parallel to the long edges of the windows. A drop of MBBA was sandwiched by the rubbed windows. Then it was slightly pressed and fastened with a plastic tape along the edges. For obtaining homeotropic alignment the windows were dipped in a 0.7 mM/l, namely somewhat smaller concentration than its critical micelle concentration, aqueous solution of cetyl-trimethylammonium bromide (CTAB), and then carefully dried to realize the surfaces covered by practically monolayer CTAB molecules. A drop of MBBA was sandwiched by the windows treated in this way.

Examination in a polarizing microscope showed completely different patterns for these two samples, which could distinguish the alignments. A characteristic threaded texture parallel to the long edges of the windows between crossed nicols was observed for the homogeneous sample, while only dark stars were observed for

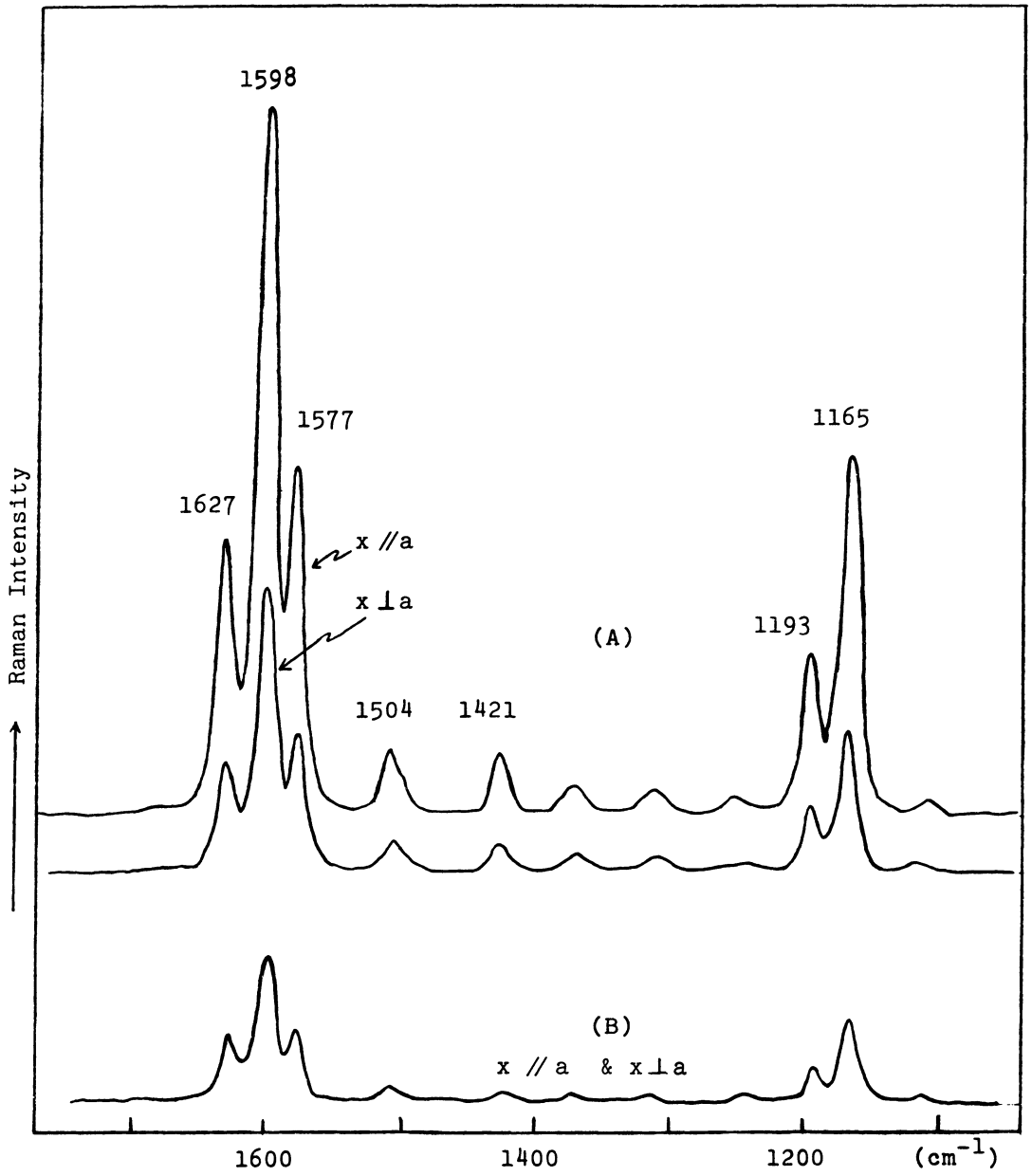

Fig. 1. Raman spectra of aligned thin (ca. 1 μm) films of MBBA; (A) homogeneous, (B) homeotropic samples.

the homeotropic sample.[1)]

Raman spectra were measured using a Jasco R-300 Raman spectrophotometer with a JEOL-04 Argon ion laser, at 25°C for the nematic phase and 45°C for the isotropic phase. All the observations for the film samples were made in the oblique settings, where the window surfaces made θ° with the incident beam (θ= 10∼60°), using 488.0 nm excitation. The direction of the long edge of the window was taken as x axis and the plane normal as z axis. The sample was irradiated by the laser beam along c axis (a, b, c mean space fixed cartesian coordinates and

z lies in the bc plane) and the scattered light was gathered to b direction.

Raman spectra observed for the thin (ca. 1 μm) film samples with a polarized incident light are shown in Fig. 1 (θ = 30°), for the 1700~1000 cm^{-1} region. (A) and (B) show the spectra for homogeneous and homeotropic samples, respectively. For the homogeneous sample the band intensities at 1598 cm^{-1} and 1577 cm^{-1} for x// a are about three times larger than those for x⊥a, while for the homeotropic sample they are almost the same for x// a and x⊥a. These spectra were independent of varying θ. The 1598 cm^{-1} and 1577 cm^{-1} bands are assigned to the benzene ring vibrations parallel to the molecular long axis of MBBA.[6,7,8] The observed Raman spectra, therefore, certainly confirm the molecular alignments suggested from the polarizing microscopic observations; the molecular long axis is parallel to the window surface for the homogeneous sample and perpendicular for the homeotropic sample.

The 1627 cm^{-1} band is ambiguously assigned to the C=N stretching vibration[6,8] or the benzene ring vibration.[7] The observed intensity ratios between the 1627 cm^{-1} and 1598 cm^{-1} bands, I(1627)/I(1598), are given in Table 1, for the film samples together with the value for the isotropic bulk. From these values the 1627 cm^{-1} band should be assigned to the C=N stretching vibration rather than the ring vibration, though there may be some vibrational couplings. It is also found that the 1598 cm^{-1} band belongs to the same symmetry species as the 1577 cm^{-1} band.

The polarization components were observed for (aa), (ac), (bc) and (ba), where (ac) means the spectrum observed with a incident and c scattered components. The relative intensities of the 1598 cm^{-1} band observed among the polarization components for θ =30° are shown in Table 2, coinciding with the theoretical expectations; I(ba)>I(bc) for homogeneous and I(bc)>I(ba) for homeotropic alignments. In this case the values depended on θ. These results also confirm the molecular arrangements suggested by the polarizing microscopic observations.

The Raman spectra of thicker samples (ca. 25 μm) showed that the molecular orientations were incomplete, though the examination in the polarizing microscope distinguished the alignments. The influence of the surface density of CTAB on the alignment of MBBA reported by Proust and Ter-Minassian-Saraga[9] has not yet been examined in this study.

These Raman results give not only an evidence for the molecular orientations suggested from the polarizing microscopic observations but also useful information for the vibrational assignments of liquid crystal molecules.

The detailed results with the low frequency spectra will be published elsewhere.

Table 1. Intensity ratios between the 1627 cm^{-1} and 1598 cm^{-1} bands, I(1627)/I(1598).

	Bulk	Film	
	isotropic	homogeneous	homeotropic
x // a	0.417	0.402	0.445
x ⊥ a		0.407	0.445

Table 2. The polarization components of the 1598 cm^{-1} band (relative values).

	Homogeneous x// a	Homeotropic x// a & x ⊥ a
(aa)	110	25
(ac)	32	12
(bc)	27	27
(ba)	63	14

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