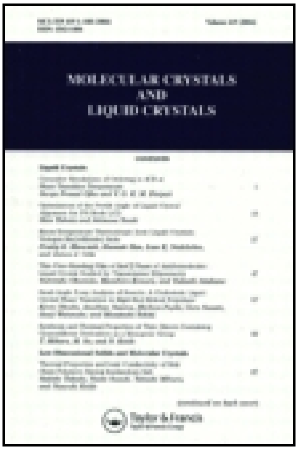

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A New Time-Resolved Raman Microspectrometer for the Study of Liquid-Crystalline Materials in Thin Cells

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A New Time-Resolved Raman Microspectrometer for the Study of Liquid-Crystalline Materials in Thin Cells

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A new Raman microspectroscope was designed for the study of thin liquid-crystalline films in glass cells. This system is based on a confocal geometry and a multi-channel liquid nitrogen cooled CCD detector. The confocal arrangement makes possible the study of volumes only a few μm^3 in size within a liquid-crystal cell with an axial resolution of 7 μm. The mutli-channel detector allows high quality spectra to be recorded in less than a second with only a few milliwatts of laser power at the sample. Using an electro-optic modulator, dynamic studies can be done on the millisecond scale or smaller. We present the first results obtained with this technique of the electrical switching of a ferroelectric liquid-crystalline low molar mass organosiloxane material.

Keywords: Raman; microspectroscopy; dynamic; liquid-crystals

INTRODUCTION

Raman microspectroscopy and Raman imaging microscopy are becoming widely used techniques for non-invasive studies of the chemical and morphological properties of various materials. Applications range from the non-destructive in-situ study of Egyptian faience[1] to the examination of phase evolution in superconducting ceramics.[2]

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The Raman effect is due to the inelastic scattering of a very small amount (1 in 10^8) of the light incident on a molecule. Each peak in a Raman spectrum corresponds to a particular vibrational (or rotational) mode within the molecule. Furthermore, the intensity of a Raman peak depends on the relative orientations of the polarizability tensor associated with the vibrational mode and the polarization of the exciting radiation. Therefore, information about the orientations of different segments of the molecule can be determined by modifying the relative orientation of the sample and the laser polarization direction.

Despite the poor efficiency of the Raman scattering effect, recent developments in holographic beam-splitters and notch-filters, together with the increasing sensitivity of CCD detectors are allowing rapid acquisitions of spectra or images with a high spatial resolution. [3] Previous studies on liquid-crystals, using an early Raman microprobe, have focussed on the electric-field re-orientation of nematic cyanobiphenyls compounds.[4-6]

In this paper we present the most recent apparatus developed in our laboratory. We will demonstrate that it offers a very high spectral and spatial resolution together with very short acquisition times. We will then show the first results obtained on a ferroelectric liquid-crystal material using Raman microspectroscopy.

DESCRIPTION OF THE MICROSPECTROMETER

A schematic of the Raman microspectrometer is presented in figure 1. An argon-ion laser with an output power of 250mW is used as the excitation radiation. The laser beam pass first into a plasma-line filter (F) to achieve a bandpass lower than 1nm. The laser excitation beam is then focussed by an objective (O1) onto a pinhole (P1) in order to remove the appearance of diffraction rings and speckle noise around the focus spot. The resulting divergent gaussian beam is than transformed into a parallel beam with the correct dimensions by a positive lens (L1). The holographic beam-splitter (BS) insures a coaxial illumination and signal collection by the same objective (O2) in the back-scattering configuration. The signal is focussed onto a second pinhole (P2) to ensure that only the signal coming from a very small volume around the focus point is transmitted. An holographic notch-filter (N) removes most of the elastically scattered light while transmitting a maximum of the Raman signal. A set of coupling optics (L3 and L4) focuses the signal onto the entrance slit of a monochromator (S) where the light is dispersed onto a liquid-nitrogen cooled CCD detector. The laser power at the sample is typically 5-10 mW.

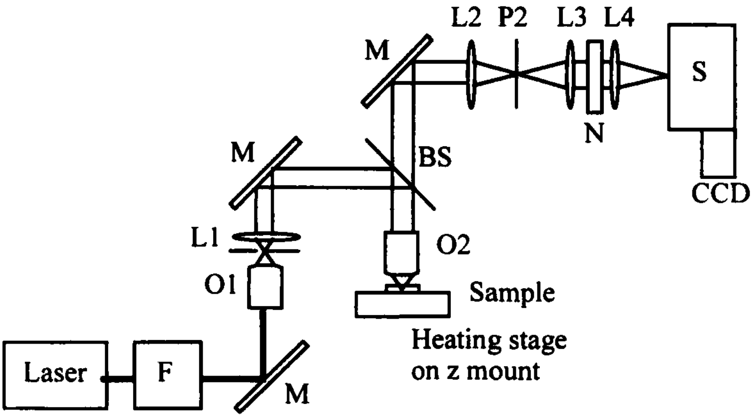

FIGURE 1. Schematic of the Raman microspectrometer, where M corresponds to mirror, see text for abbreviations.

RESULTS

We will first demonstrate the high spectral and spatial resolution of the spectrometer. We will then present some results obtained during dynamic measurements of the electrical switching of a ferroelectric liquid-crystal material.

Spectral resolution of the spectrometer

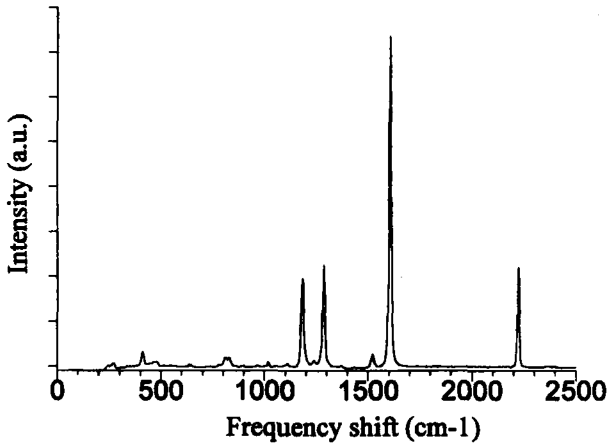

FIGURE 2. Raman spectrum of 5CB

Figure 2 shows a Raman spectrum of n-pentyl cyanobiphenyl (5CB) taken in the nematic phase in a few seconds with less than 5mW of laser power at the sample. The positions and assignments of the Raman peaks are detailed in table 1. Previous apparatus required acquisition times between several tens of minutes and an hour in order to achieve a comparable signal over noise ratio.[7]

Wavenumber (cm^{-1})	Assignment
412	Ring vibration
812	Ring breathing vibration
830	Alkyl chain vibration
1020	Aromatic C-H in-plane deformation
1110	Alkyl chain vibration
1182	Aromatic C-H in-plane deformation
1238	Ring vibration
1286	C-C stretch of biphenyl link
1524	C-H deformation of pentyl chain
1605	C-C stretch of aromatic rings
2222	CN stretch

TABLE 1. Position and assignment of 5CB Raman peaks.

Spatial resolution of the spectrometer

Using a confocal arrangement one may expect a high spatial resolution due to the rejection of the out of focus signal at the pinhole. We checked the resolution of our apparatus using a very thin (1μm) layer of 5CB sandwiched between two thick (1mm) glass slides in order to be as close as possible to reality. The sample was moved in one micron increments between each spectra. Figure 3 shows the value of the intensity of the 1605 cm^{-1} peak as a function of the displacement. The resolution is defined as the full width at half maximum (FWHM).

With a 100 magnification microscope objective having a numerical aperture of 0.8 and a detection pinhole of diameter 50 μm the resolution is close to 7μm.

Time-resolved studies

One restriction linked to the use of a CCD detector is the relatively slow response time compared to that of a PMT. To circumvent this problem we decided to use an electro-optic modulator consisting of two high-voltage pulse generators and a four terminator Pockell cell. With this setting, one can set the modulator to transmit the light at a defined time and for a very short period. An electric pulse from a signal generator can trigger this process. We will show in the next section how this system can be used to follow the electrical switching of a ferroelectric compound.

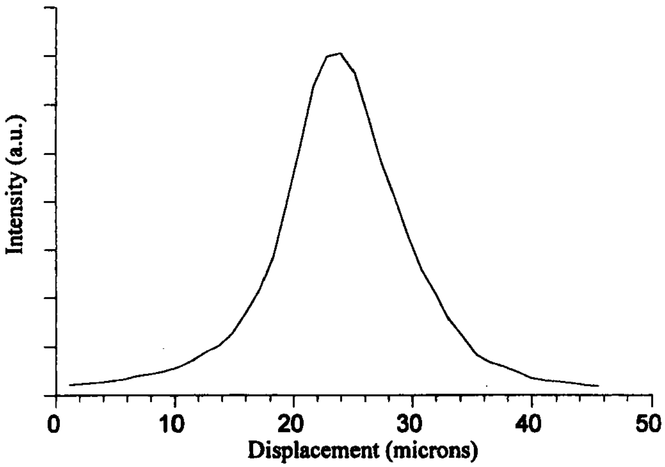

FIGURE 3. Measurement of spatial resolution.

Study of the switching of a ferroelectric liquid-crystal

We investigated the behaviour of a ferroelectric low molar mass organosiloxane liquid-crystal under an electric field. The mesogenic units attached to the tri-siloxane chain are based on a biphenyl benzoate.[8] We applied a square voltage ($V_{p\text{-}p}$=180 V, 10 Hz) to a 7.5 μm cell and measured the intensity of the 1605 cm^{-1} Raman peak corresponding to the C-C stretch of aromatic rings.

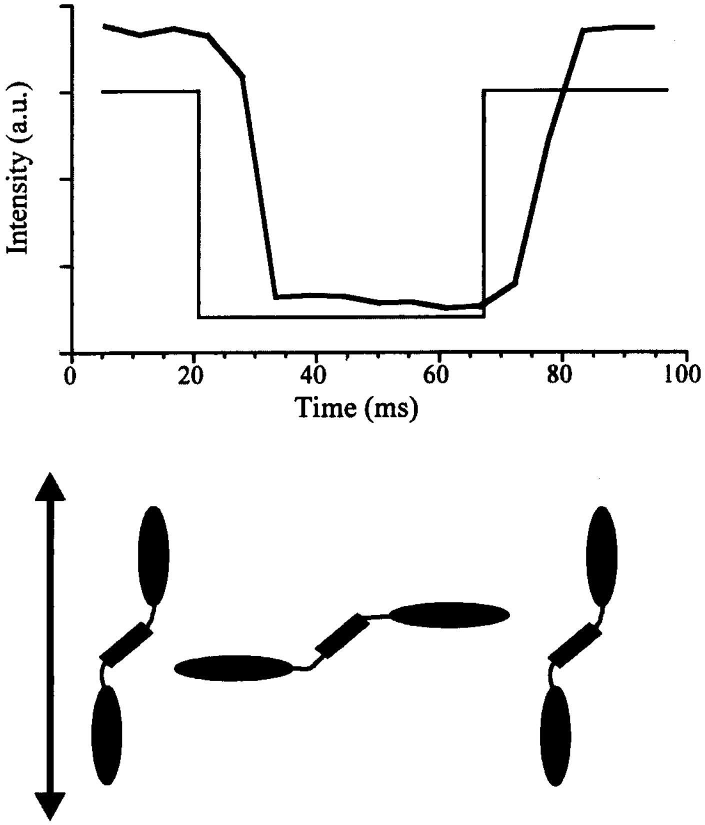

FIGURE 4. Intensity of the 1605 cm^{-1} peak and voltage (square signal) versus time and relative orientation of the mesogens. The arrow indicates the direction of the laser polarization.

The time resolution was set to 5 ms and each sample time slot took a hundred seconds to record. The result is plotted in figure 4 together with the deduced relative orientation of the mesogens and the polarization of the exciting beam. When the voltage is positive the mesogenic groups are oriented parallel to the exciting laser polarization and the Raman signal is maximal. On the other hand when the voltage is negative the mesogenic groups are orthogonal to the laser polarization and the Raman signal is minimal.

CONCLUSION

We have demonstrated that Raman microspectroscopy delivers valuable information on the arrangement of the different segments of a molecule. This is done in only a few seconds and can be performed on a μm^3 sample within a liquid-crystal cell with no loss of spectral or spatial resolution. Time-resolved studies provide an insight into the sub-molecular dynamics of liquid-crystalline systems with a time resolution of less than one millisecond.

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