

# Study of Liquid Crystal Absorbed On Nano-Roughened Ag and Au Electrodes by SERS

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## ABSTRACT

By using Surface-Enhanced Raman Scattering, We studied the orientation of liquid crystal 5CB absorbed on nano-roughened Ag and Au Electrodes. Our results firstly suggest that the orientation of LC 5CB absorbed on nano-roughened Ag electrode is different from that of Au electrode. This implies that the interaction between LC 5CB and Ag is different from the interaction between LC 5CB and Au. The conclusion is that the orientation of LC 5CB absorbed on nano-roughened Ag electrode is perpendicular, and the orientaiton of LC 5CB absorbed on nano-roughened Au electrode is more complicated, including parallel, perpendicular and tilted.

**Keywords:** Liquid Crystal 5CB, SERS, Orientation

## INTRODUCTION

The interaction between the LC molecules and surface could induce orientational order and hence, affect bulk-alignment properties of LC cells<sup>1</sup>. Therefore it is important that we understand the mechanism responsible for this surface-induced LC alignment. It is generally believed that molecular interactions between LC and surfaces rather than the micro-groove plays the key role in affecting the LC alignment. This suggests the importance of knowing the molecular orientation. A clear understanding of the correlation between surface and LC alignment is still missing, suggesting the need of further investigation with other surface sensitive experimental techniques<sup>2</sup>.

In this paper, we report the orientation study of LC 5CB absorbed on nono-roughened Ag and Au electrodes with surface-sensitive techniques, surface-enhanced Raman scattering(SERS). We found that the molecular orientation of 5CB at the surfaces of nono-roughened Ag and Au electrodes were different. This difference is presumably derived from the differences in the electronic structure of the electrode surfaces.

Vibrational spectroscopy is known to be an effective probe to access the nature of chemical bonding, interaction, conformations and even orientation of molecules. However, normal infrared or Raman vibrational spectroscopy is not surface-specific. It was found in 1974 that the intensity of Raman scattering from molecules adjacent to a roughened silversurface can be enhanced by as much as  $10^6$  times<sup>3,4</sup>. The enhancement decreases rapidly as a function of distance away from the silver surface, making this Raman scattering particularly surface-sensitive. SERS is now considered as one of the major techniques in the area of surface characterization. Here we report the application of SERS to the orientation study of LC 5CB absorbed on nono-roughened electrodes.

## EXPERIMENT

5CB, shortened form of 4'-cyano-4-5-alkylbiphenyls, is a typical nematic liquid crystal. Fig. 1 is its chemical structure.

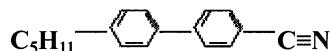


Fig. 1 Chemical structure of 5CB

Nono-roughened Ag and Au electrode surfaces were dealt with electrochemical activation. All the experiments were done under room temperature.

The Raman spectra were obtained using a confocal microprobe Raman system (LabRam I from Dilor, France. The micro-scope attachment is based on an Olympus BX40 system and uses a 50× long working-length objective(8mm) so that the objective will not be immersed in the electrolyte. A holographic notch filter was equipped to filter the exciting line, and two selective holographic gratings(1800 Fig. 2a, 2b and 2c show normal Raman spectrum, SERS spectrum on nano-roughened Ag electrode surface and SERS spectrum on nano-roughened Au electrode surface. The exciting wavelength is 632.8nm. Comparing of these spectra, we find that the Raman spectra on electrode surface have much difference. Gratings (1800 g/mm and 300 g/mm) were employed for different purposes of work. An air-cooled 1024×256 pixels CCD (Wright, England) operating in the MPP mode at -60°C was used as the detector. The exciting wavelength was 632.8nm from an air-cooled He-Ne laser with a power of 16mW and a spot of ca. 3 μm on the surface. The slit and pinhole in experiment were 100 and 400 μm, respectively. With the 1800g/mm holographic grating, the spectral resolution is 1.5-3.0cm<sup>-1</sup>, varying with the spectral region.

## RESULTS AND DISCUSSION

Hence from the bulk Raman spectrum, and the Raman spectrum on different electrode surface are also not the same. The latter implies different interactions between LC 5CB and Ag and Au electrode surfaces.

Comparing Fig.2b with Fig.2a, we find that in the SERS spectra of 5CB absorbed on nano-roughened Ag electrode surface, only several major vibrational modes emerge. They are 406cm<sup>-1</sup>, 832cm<sup>-1</sup>, 1183cm<sup>-1</sup>, 1284cm<sup>-1</sup>, 1607cm<sup>-1</sup> and 2232cm<sup>-1</sup>, identified as ring vibration, alkyl chain vibration, C-H in-plane distortion vibration, C-C stretching vibration, C≡N stretching vibration, respectively. In addition, only 832cm<sup>-1</sup> of all the vibration modes relevant to the alkyl chain emerges. And the band frequencies and relative order are fairly good agreement with the normal Raman spectrum. However, the relative intensity of all the other bands compared to the most intensive band of 1607 cm<sup>-1</sup> decrease, among of them, the relative intensity of C≡N stretching vibration reduce more than the others. In Fig.2b, only a vibration mode of 832cm<sup>-1</sup> is detected among of all the alkyl chain vibration, this can probably result from the distance affect. The long alkyl chain C<sub>5</sub>H<sub>11</sub>- is non-polar and no interaction induces between it and the nano-roughened Ag electrode surface atom. So it is far away from the nano-roughened Ag electrode surface. And C≡N- has strong polarity<sup>5</sup>, interacts with the nano-roughened Ag electrode surface atom, forms Ag-N bond, so that the relative intensity of C≡N stretching vibration reduce the most. Based on the selection rules of SERS for molecules absorbed on metal surfaces, molecular vibrations involving motions perpendicular to the surface should be enhanced best in the spectra, while those involving motions

parallel to the surface weakened. The drastic increase in the intensity of the aromatic in-plane stretching at  $1607\text{cm}^{-1}$  indicates that the phenyls are perpendicular to the nano-roughened Ag electrode surface. In summary, the chain CN- interacts with the Ag atom, forms Ag-N bond, and the long alkyl chain  $\text{C}_5\text{H}_{11}$ - far away from the nano-roughened Ag electrode surface, and the phenyls are perpendicular to the surface, so the LC 5CB molecules absorbed on the nano-roughened Ag electrode are perpendicular to the electrode surface. The sketch map of such absorbability shows in Fig.3.

Comparing Fig.2c with Fig.2a and Fig.2b, besides all the bands of SERS on Ag electrode surface emerge, we also observe  $807\text{cm}^{-1}$ ,  $900\text{cm}^{-1}$ ,  $2138\text{cm}^{-1}$ ,  $2919\text{cm}^{-1}$  and  $3062\text{cm}^{-1}$ , identified as alkyl chain vibration, alkyl chain vibration,  $\text{C}\equiv\text{N}$  stretching vibration,  $\text{CH}_2$  stretching, CH stretching, respectively. We find that more vibration bands correlative with the  $\text{C}_5\text{H}_{11}$ - vibration are enhanced. These suggest that the SERS of 5CB absorbed on nano-roughened Au electrode surface is more complicated than that of nano-roughened Ag electrode surface and the interactions are different between 5CB molecules and Ag and Au electrode surfaces. All the bands of SERS on Ag electrode surface also emerge in the SERS of Au electrode surface, so there are some 5CB molecules perpendicular to the nano-roughened Au electrode surface. More alkyl chain vibrations get enhanced, this suggests that there are some alkyl chain close to the electrode surface. And the emergence of  $2138\text{cm}^{-1}$  bands, we think that there exists another interaction between 5CB molecules and Au surface atom. The interaction we think is so-called Pi-absorbability, derived from the interaction of phenyl and Au electrode surface atoms. In a word, we think that 5CB molecules absorbed on the nano-roughened Au electrode, is orient random, including perpendicular, parallel and tilted. The parallel absorption sketch map shows in Fig.4.

## CONCLUSION

The orientation of LC 5CB absorbed on nano-roughened Ag and Au electrode surfaces were studied by using SERS with the exciting wavelength of  $632.8\text{nm}$ . Our results firstly suggest that the orientation of LC 5CB absorbed on nano-roughened Ag electrode is different from that of Au electrode. This implies that the interaction between LC 5CB and Ag is different from the interaction between LC 5CB and Au. These results may shed some light on the understanding of the interaction mechanism between molecular and nano-roughened electrode surface.

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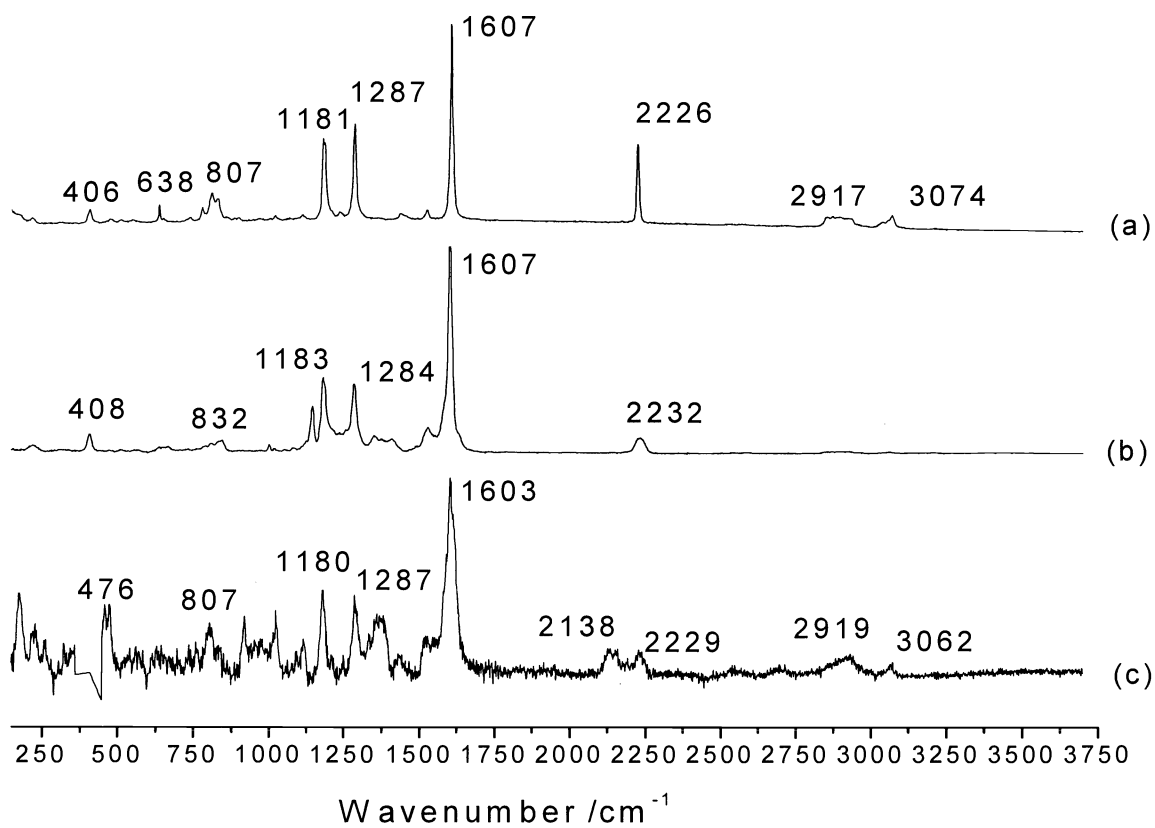


Fig. 2 Raman spectrum of 5CB.

(a)Normal Raman Spectra,(b)SERS on roughened Ag electrode,

(c)SERS on roughened Au electrode.The excitation line was 632.8nm.

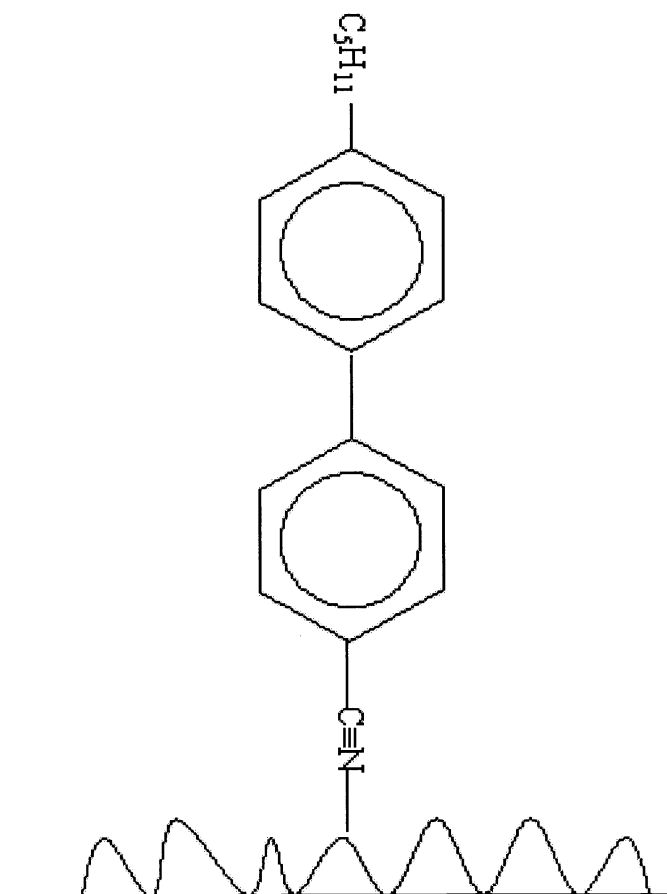


Fig.3 the perpendicular absorb sketch map of 5CB on electrode surface

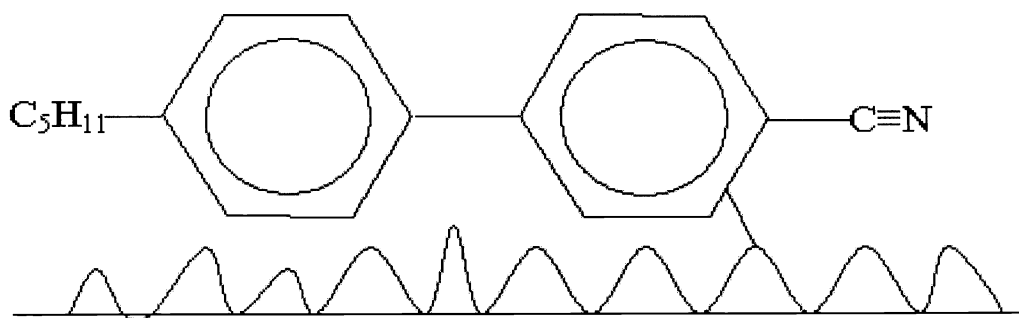


Fig.4 the parallel absorb sketch map of 5CB on electrode surface