國 立 交 通 大 學

電 機 資 訊 學 院
光 電 工 程 研 究 所

博 士 論 文

液晶薄膜場致轉向動態之時析振動光譜研究

Multichannel Time-Resolved Vibrational Spectroscopy of the Field-Induced Reorientation Dynamics of Liquid Crystal Thin Films

研 究 生: 施文慈

指導教授: 黃中垚 教授

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合於博士資格標準、業經本委員會評審認可。

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submitted by Wen-Tse Shih in partial fulfillment of the requirements of the degree of DOCTOR OF PHILOSOPHY and recommend its acceptance.

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液晶薄膜場致轉向動態之時析振動光譜研究

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摘要

不論是在液晶物理的研究上，或是在液晶元件的發展上，場致分子轉向的動態過程都是一個重要課題。本論文利用偏振傅立葉轉換紅外光譜及拉曼光譜，研究向列反向扭轉液晶及表面穩定鐵電性液晶的場致分子轉向動態過程。在紅外吸收光譜量測方面，我們建構了一套多頻道時析系統進行高效率的動態光譜量測，並應用二維相關光譜技術分析量測的結果。對於二維相關光譜分析與異向性液晶薄膜的分子官能基排列及轉向之間的關連，也做了理論的模擬與討論。

由向列反向扭轉液晶的研究發現，液晶分子在沿著分子長軸方向會發生侷限性的旋轉，電光反應之亮度上升和下降時間分別是6和1.6毫秒，場致轉向的動態過程中液晶分子的運動並非剛體旋轉。

在表面穩定鐵電性液晶方面，我們觀察了鐵電性液晶純材料CMHCB在結晶相和鐵電相的分子構形及排列。二維相關光譜分析的結果反映出鐵電相中存在的Goldstone mode，而溫度變化引起的重新排列與分子官能基有關。場致轉向的過程始於分子內的運動，這個過程持續約不到10微秒。此外也發現CMHCB對於電場極性的反應並不對稱，這也表示在分子尺度中，相對於分子主軸的順時針與逆時針對稱性並不存在。

我們也研究了另一個鐵電性混合材料的場致轉向過程。從二維相關光譜分析結果可以看出，外加電場會抑制Goldstone mode。與前述的鐵電性純材料

相類似，此一表面穩定鐵電性混合材料的樣品對於電場的極性反應也不對稱，同樣在分子尺度中，相對於分子主軸的順時針與逆時針對稱性並不存在。瞬態過程中，場致分子轉向始於分子內部的運動，此一過程約持續10微秒，之後分子內部運動由單一分子座標內的官能基，傳遞到其他分子座標內的官能基。而分子官能基如C-O-C，C=C，及C-H均沿著傾斜的角錐面，以不同角速度做相關但非一致性的旋轉。

本論文的研究結合了多頻道時析系統的分子振動光譜量測與二維相關光譜分析技術，這樣的方法對於場致動態分子形變、分子排列、次分子動力學以及分子與環境交互作用等相關研究，能夠有效率的觀測分析大量訊息，確實是個非常有用的方法。

Multichannel Time-Resolved Vibrational Spectroscopy of the Field-Induced Reorientation Dynamics of Liquid Crystal Thin Films

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Abstract

The field-induced molecular reorientation dynamics of a nematic twisted pi-cell and surface stabilized ferroelectric liquid crystals (SSFLC) had been studied with time-resolved polarized Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy. We constructed a multichannel time resolving system to perform the FTIR measurements and employed two dimensional (2D) correlation techniques to analyze the obtained IR spectra. The different information obtained from the 2D correlation technique and 2D hetero correlation technique was elucidated. The effects of the alignments and orientations of functional groups in an anisotropic film on the 2D correlation were also discussed.

The alignment of the LC molecules in a nematic twisted pi-cell was revealed. The results suggest that the molecules undergo a restricted rotation about the molecular long axis. The rise and decay times of the electro-optical response were found to be 6 ms and 1.6 ms, respectively. In the switching dynamic process, the LC molecules in the twisted pi-cell do not rotate like a rigid molecule during the field induced reorientation process.

A neat ferroelectric liquid crystal CMHCB in an SSFLC cell was studied. The molecular conformations and alignments of CMHCB in the K phase and SmC* phase were studied. The 2D IR correlations clearly exhibit Goldstone mode in the SmC* phase. The phase transition-induced re-arrangement was found to be

dependent on the molecular fragments. We demonstrated that the 2D IR correlation technique can reveal the field-induced collective reorientation of the molecular segments in the CMHCB. The reorientation process starts from the chiral part with an intramolecular motion, which proceeds in less than 10 μsec. In addition, we found an asymmetry in the response of the CMHCB to electric field polarities, indicating that the clockwise–anticlockwise symmetry about the cone axis is broken.

The molecular motion of an SSFLC mixture during a field-induced reorientation process was studied. The 2D IR correlation technique clearly reveals that the thermal fluctuations in the azimuthal angle of the FLC director about a tilt cone in the SmC* phase with unwound structure are suppressed by an applied electric field. In addition, an asymmetry in the response of the surface stabilized FLC mixture to positive and negative driving pulses was also revealed in the 2D IR correlation analysis, indicating that similar to CMHCB, the clockwise–anticlockwise symmetry about the cone axis is broken at the molecular level in the FLC mixture. In a transient situation, the field-induced reorientation process was found to start with an intramolecular motion, which proceeds in about 10 μsec. The intramolecular motion then propagates from the fragments attached to a single molecule to the ones belonging to different molecular coordinates. The molecular segments of C–O–C, C=C, and C–H stretch modes were found to rotate about a tilted cone with different angular speeds in a correlated but non rigid way.

The combination of multichannel time-resolved vibrational spectroscopy and 2D correlation spectroscopy demonstrated in this thesis shall be useful for the studies of field-induced transient molecular deformations and alignment, submolecular dynamics and molecular-environment interactions.

Contents

List of Tables

List of Figures