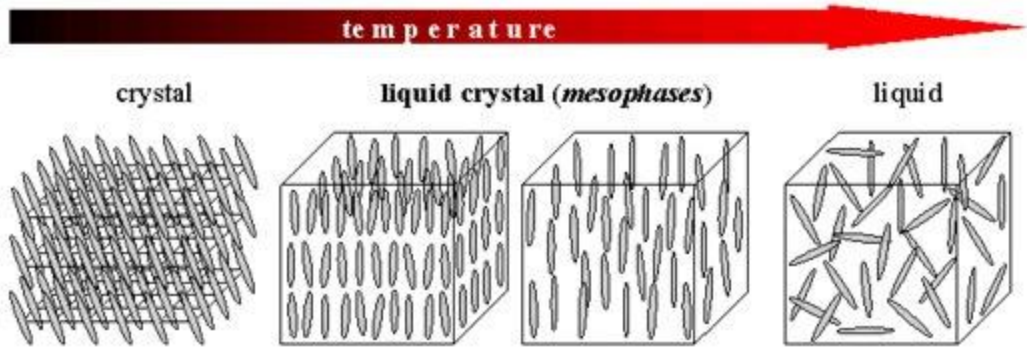
Study of Molecular Dynamics in Two Liquid Crystal Dimers using Laser Raman Spectroscopy

Dr. P. R. Alapati
Professor, Department of Physics
North Eastern Regional Institute of Science and Technology
Nirjuli, Itanagar 791 109
Arunachal Pradesh
INDIA

Collaborators

A. Bhattacharjee
D. Bhuyan
T. Kiranmala Devi
B.Gogoi

Liquid Crystals



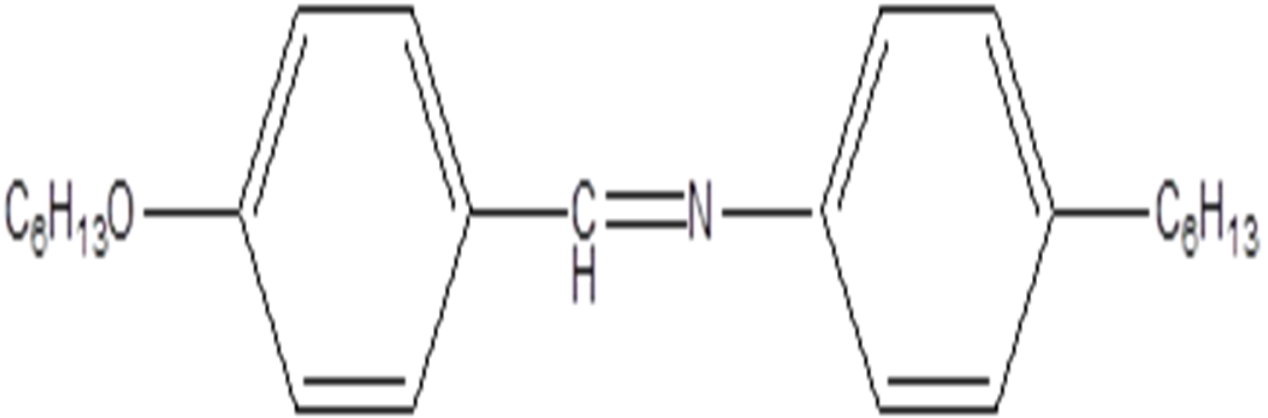
Types Of Liquid Crystals

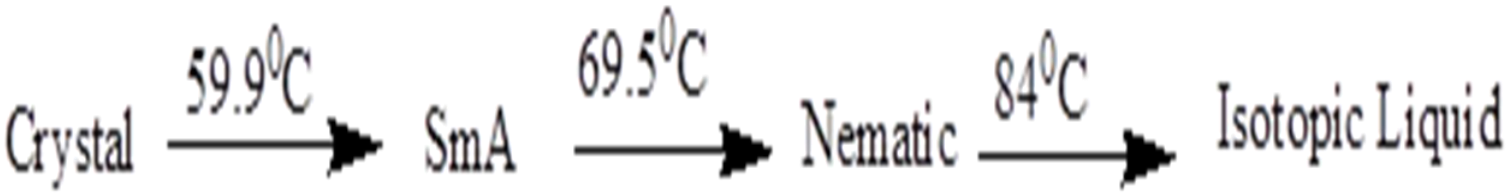
A. Thermotropic Liquid Crystals

1. Calamitic Liquid Crystals
2. Discotic Liquid Crystals
3. Ferroelectric Liquid Crystals
4. LCPs and PDLCs
5. Defect Phases

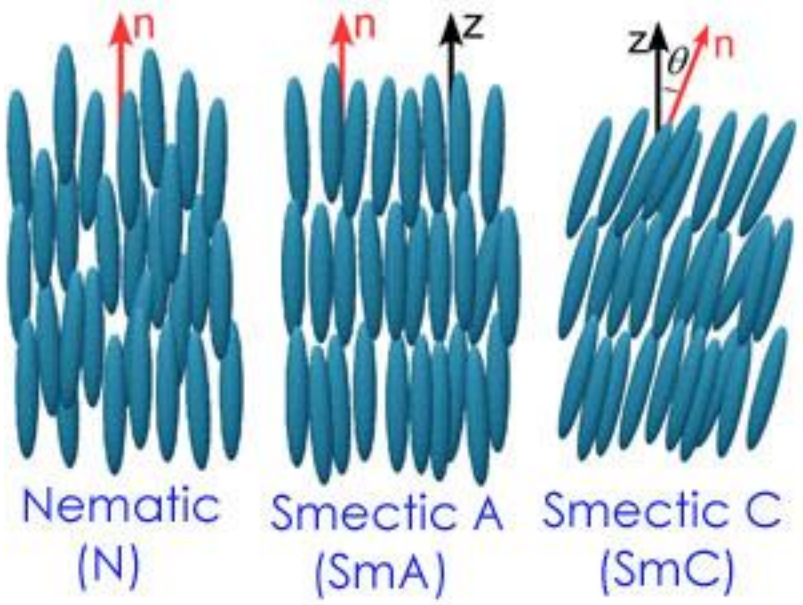
B. Lyotropic Liquid Crystals

Types of Th. LC Molecules (Calamitic)

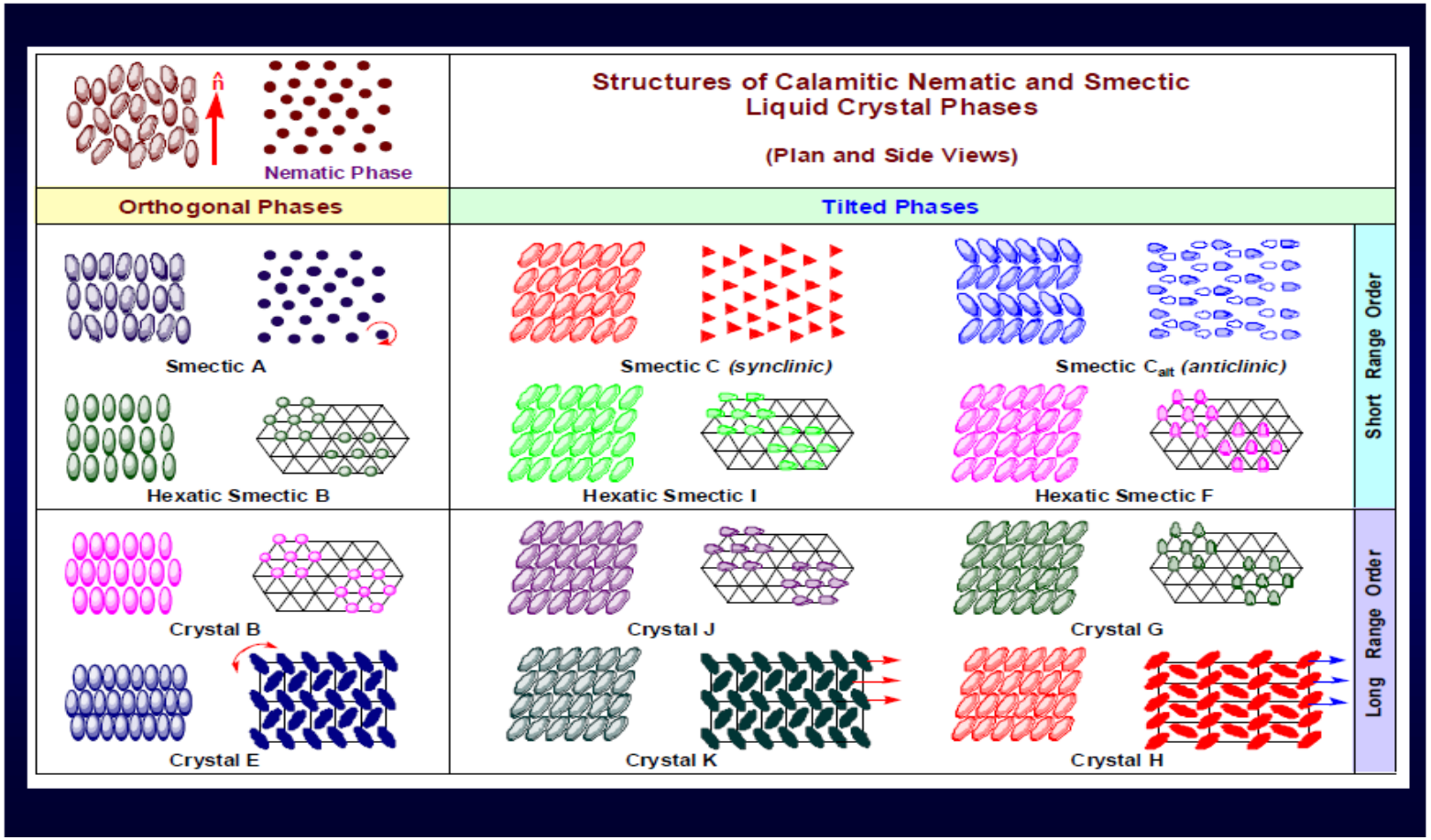




Nematic - Sm A – Sm C Phases

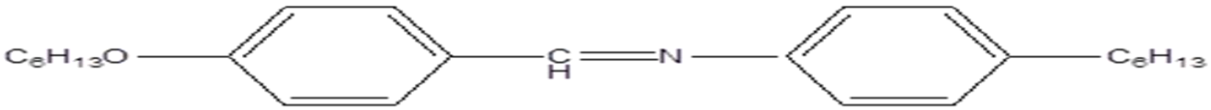


Other Calamitic Liquid Crystal Phases

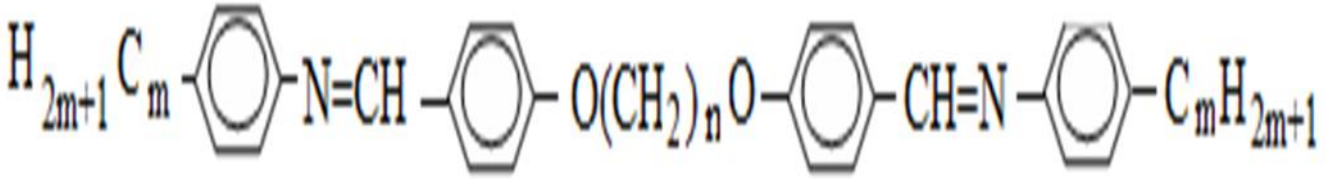


I-N-SmA-SmC-SmB(Hex)-SmI-SmB(Cr)-SmF-SmJ-SmG-SmE-SmK-SmH

Liquid Crystal Dimers



Crystal $\xrightarrow{59.9^0C}$ SmA $\xrightarrow{69.5^0C}$ Nematic $\xrightarrow{84^0C}$ Isotopic Liquid



- Importance LC Dimers
- They act as model systems for understanding the phase behaviour and physical properties of main chain Liquid Crystal polymers
- Rich in smectic polymorphism
- Exhibit different phase behaviour w. r. t the appearance of nematic phase as compared with their precursors (monomers) ----- (motivation for this work)
- Exhibit strong odd – even effect in transition temperatures and entropy values of isotropic – mesophase transition

Use of Laser Raman Spectroscopy

Useful tool in the investigation of vibrational dynamics of liquid crystals for following reasons

1. Because the phase transitions are reflected as variations in measurable parameters of certain vibrational modes of the system

2. The measurement and analysis of line widths and peak positions yield information about the structure and dynamics of the system undergoing phase transition

3. Integrated intensity provides crucial information about the fluctuations of some physical quantities undergoing changes during phase transition

Experimental Details

- The compounds studied using Raman studies are 6.O6O.6, 6.O12O.6, 7.O4O.7 and 7.O6O.7
- The Raman spectra, at different temperatures, were recorded with a Horiba Triax Imaging (Jobin Yvon) monochromator equipped with a CCD detector (Jobin Yvon)
- Chosen spectral region :1000 – 1735 cm^{-1}
- Excitation source uses was a 442 .0 nm He – Cd laser
- Low laser power of 20 - 30 mW was used to prevent sample from laser heating
- Spectra were fitted and analysed using GRAMS software
- Samples were sealed in 0.5 mm quartz capillary tubesin an inert atmosphere
- Temperature range :

  RT (crystalline phase) – 130^{o}C for 6.O6O.7 (isotropic phase)

  RT (crystalline phase) – 180^{o}C for 6.O12O.6 (isotropic phase)

Phase sequence and Transition temperatures of 6.O6O.6 and 6.O12O.6 (from Differential Scanning Calorimetry and Polarizing Thermal Microscopy)

- 6.O6O.6

  Crystal – SmF : 124^{o}C

  SmF – SmA : 137.6^{o}C

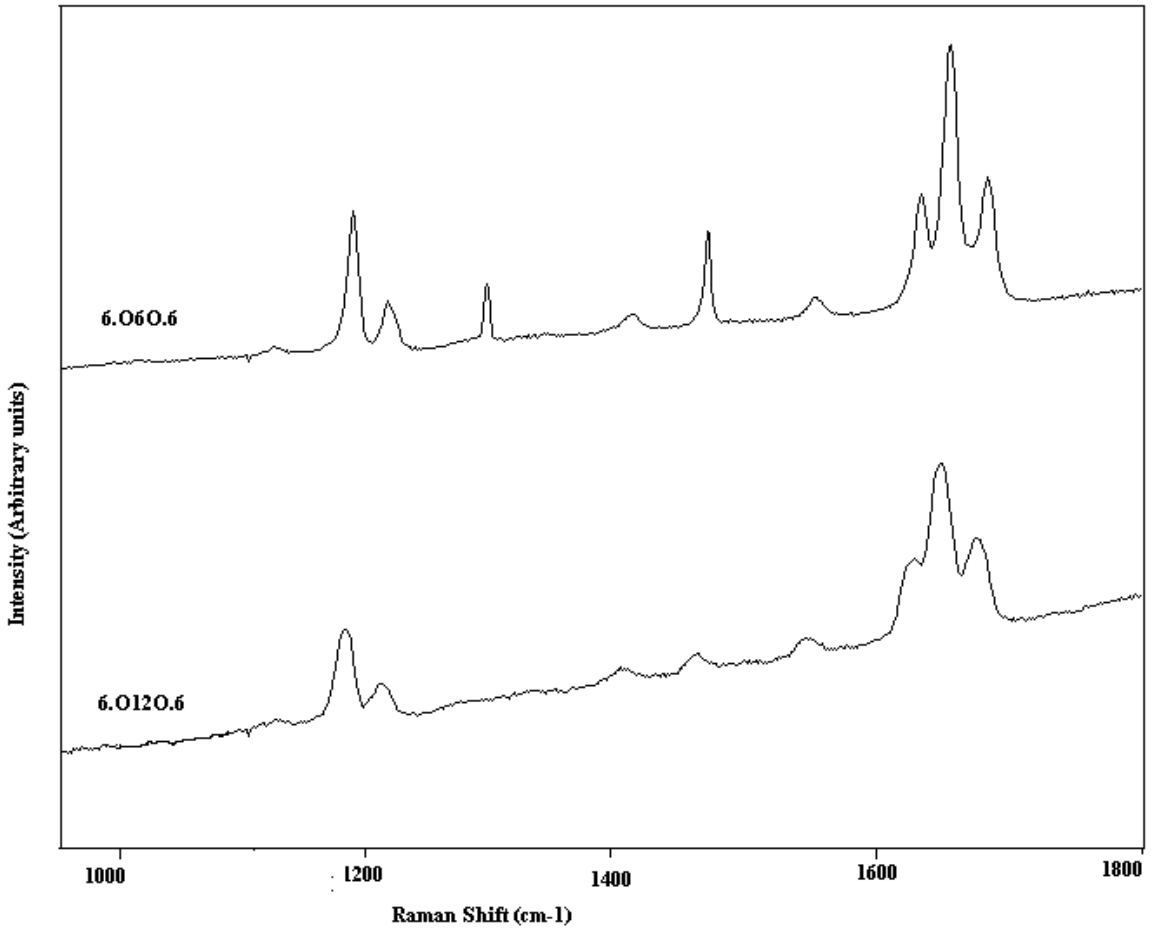
  SmA – Isotropic : 180^{o}C

- 6.O12O.6

  Crystal – Nematic : 129.1^{o}C

  Nematic – Isotropic : 132^{o}C

Comparison of Raman spectra of 6.O6O.6 and 6.O12O.6 at RT



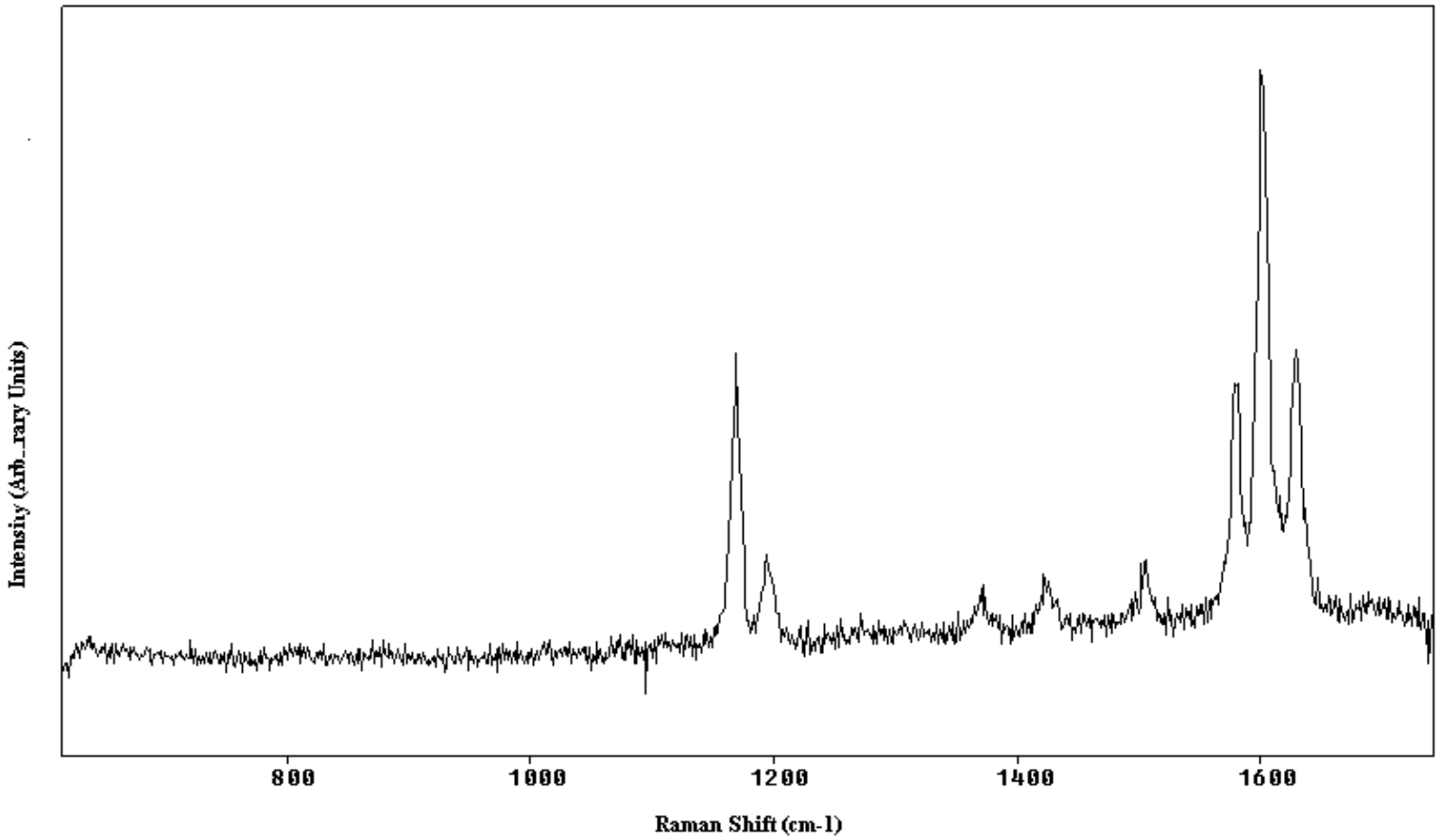
Comparison of Raman spectra of 6.O6O.6 and 6.O12O.6 at RT Contd….

Band position of 6.O6O.6 (cm^{-1})	Band assignments	Band position of 6.0120.6(cm^{-1})
1142	Aromatic C-H in plane bending mode.	1140
1172	Aromatic CO stretching mode	1169
1242	Aromatic C-N stretching mode.	
1352	CH2 twisting mode	1346
1410	CH2 deformation mode	1401
1491	Semi Circular stretching of aromatic ring	1486
1572	Quadrant stretching mode of the aromatic ring.	1565
1595	Quadrant stretching mode of the aromatic ring.	1590
1621	C=N stretching mode.	1616

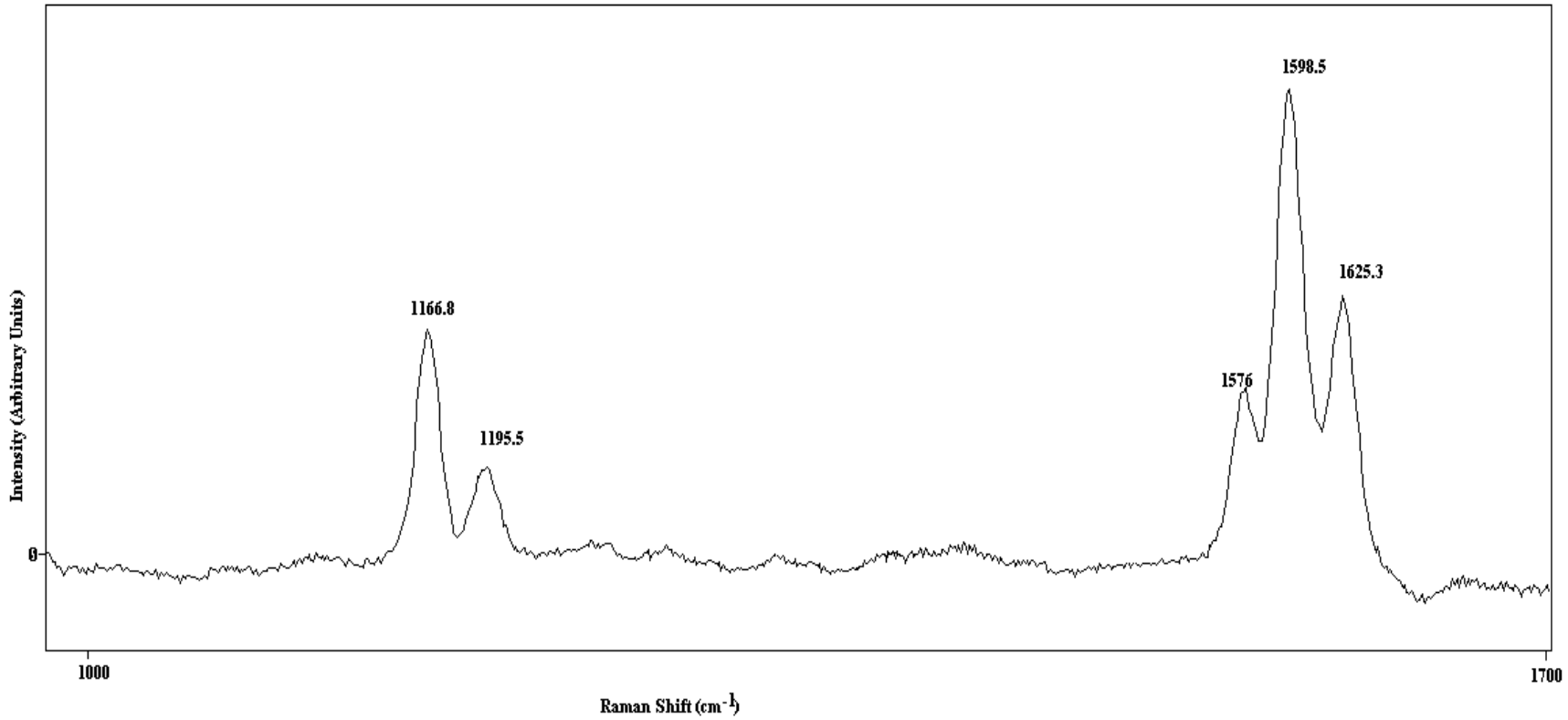
Comparison of Raman spectra of 6.O6O.6 and 6.O12O.6 at RT Cond..

- In the Raman spectra of 6.O6O.6 two sharp peaks appear at 1242 cm^{-1} (Aromatic C-N stretching mode) and 1410 cm^{-1} (CH_2 deformation mode) and two weaker bands at 1352 cm^{-1} (CH_2 twisting mode) and 1491 cm^{-1} (semi circular stretching of aromatic ring)
- In 6.O12O.6 the peak at 1242 cm^{-1} disappeared altogether and the peak at 1410 cm^{-1} has slightly weakened. However, the other two weak bands at 1352 cm^{-1} and 1491 cm^{-1} remained same in both compounds.
- These sharp peaks in 6.O6O.6 are unlike those observed in any dimeric liquid crystal
- Peaks at these positions are generally observed in monomers like MBBA, TBBA, TBDA, etc.
- Differences are also observed in the other peak positions. All the other bands appearing in the spectrum of the compound 6.O6O.6 show a respective downward shift in the spectrum of 6.O12O.6.
- The downward shift of the peak positions for different modes indicates a decrease in energy of the various bonds in 6.O12O.6 which is attributed to the averaging effect of the long alkyl spacer.
- Appearance of these bands was also observed in 7.O6O.6 (shown in the next slide) which were absent in the lower spacer length dimers such as 7.O4O.7

Raman Spectra of 7.O6O.7



Raman Spectra of 7.O4O.7



Conclusions

- Usually it is observed that in case of the calamitic liquid crystalline monomers the lower homologues exhibit nematic phases and the higher homologues exhibit the smectic phases. The case is just the reverse in case of liquid crystalline dimers where the higher spacer length dimers exhibit the nematic phase and the lower spacer length dimers exhibit the smectic phases

- The appearance of bands at 1242 cm^{-1} , 1410 cm^{-1} , 1352 cm^{-1} and 1491 cm^{-1} correspond to methylene unit in both 6.O6O.6 and 6.O12O.6 suggests that the molecule here attains some rigidity which may be due attainment of a specific shape or conformation which is similar to those of monomeric compounds such as MBBA, TBBA, TBDA etc. which must be the reason for the appearance of nematic phase in dimers of longer spacer length.

Thank You