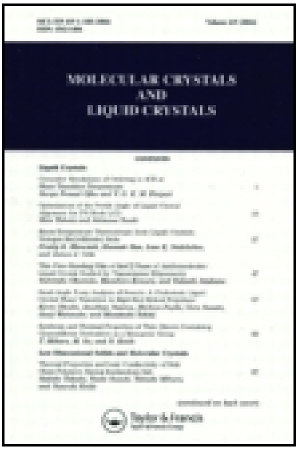

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MOLECULAR MOBILITY IN LIQUID CRYTALLINE POLYMERS FROM VIBRATIONAL SPECTROSCOPY.

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Abstract. It is shown that the vibrational infrared and Raman spectra of molecules containing polymethylene chains provide direct information on local and collective chain mobility.The experimental data to be used are frequencies,intensities and band shapes (or band widths).

INTRODUCTION

We wish to present in this paper the concepts developed and the techniques presently available for improving the use of vibrational infrared and Raman spectroscopy in the understanding of molecular structure and dynamics of liquid crystals and liquid crystal polymers.While chemists commonly interpret the observed spectra of these very complex systems on the basis of the well known spectroscopic correlations ,many spectroscopic signals are neglected ,thus undermining the importance and the usefulness of vibrational spectroscopy in this field of material science.

1) Vibrational frequencies.Polymers in their crystalline and ordered state can be treated as simple one-dimensional crystals and their 1-d lattice dynamical analysis can be routinely carried out with present computing programs[1]. One can extract from these calculations frequencies and shapes(vibrational displacements) of the normal vibrations (phonons) of the 1-D lattice. k=0 phonons may be Infrared and/or Raman active,thus allowing to identify in the spectra the bands due to the "perfect and ordered" part of the material. Dispersion curves and one-phonon or multi-phonon density of states provide the tools for understanding data from neutron scattering experiments[1,2].

Polymers in general,however, and especially liquid crystal polymers, never show only a well ordered phase, but chemical defects as well as structural and conformational defects densely populate the material. The development of lattice dynamical treatments with the consequent availability of computer programs allow at present to predict where in the spectrum one may expect to find spectroscopic signals characteristic of a given kind of strucural defect[2]. The most common conformational kinks in a polymethylene chain show characteristic bands in Infrared or Raman such as their existence can be easily be verified.Kinks of the type G, GG, GTG, GTG' and GGTGG have been identified in polymethylene systems and phase transitions have been studied in terms of local conformational dynamics[3].

As an application of what illustrated above we report in fig 1 the case of the temperature dependent infrared spectrum of 4-dodecyl, 4'cyano byphenyl through K-S_A and S_A-I phase transitions[4]. In fig.1 the difference spectrum is reported in the structurally sensitive spectral range from 1420 to 1300 cm^{-1}.In this range the conforma-tional kinks mentioned above can be revealed from the apperance of characteristic absorptions due to vibrational motions topologically localized on each of the defects. Fig. 1 tells us that: i)in the K phase the dodecyl chain is strictly trans planar ,ii)the chains remains planar until K-S_A phase transition,iii) the chain immediately collapses in a liquid like state at the transition ,GTG',GG and GTG kinks are observed.;iv)the population of rotational isomers does not change significantly in the S_A phase and only slightly at the S_A-I transition.

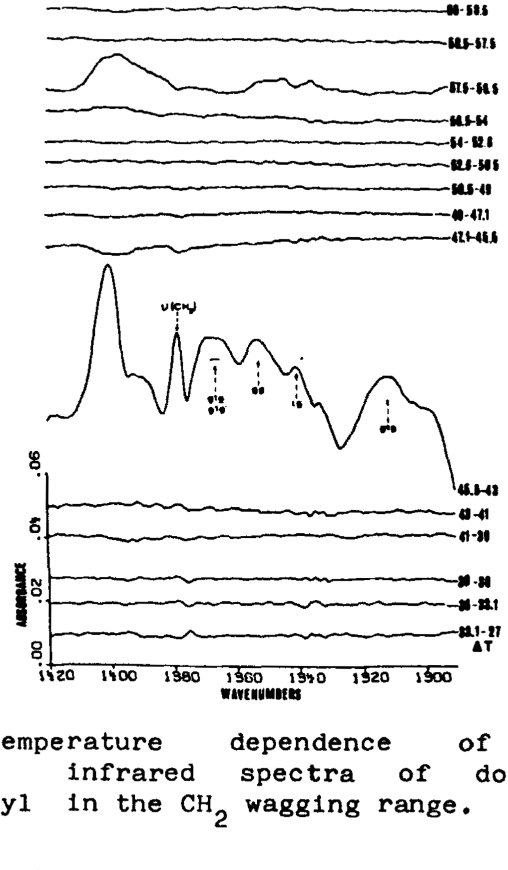

FIGURE 1. Temperature dependence of the difference infrared spectra of dodecyl-cyano-biphenyl in the CH_2 wagging range.

For conformational analysis of polymethylene chains one can also use the following additional and very important concepts :

a)When by selective deuteration one CH_2 group is replaced by a CD_2 the CD_2 rocking motion is predicted(and observed)at 615 cm^{-1} if the conformation is Trans on both sides; if $(G)CD_2(T)$ or $(G)CD_2(G)$ occur, band are expected (and observed) near 650 and 670 cm^{-1} respectively[5,6]. On can then map the conformational topology of the alkyl chain site by site[7].

b)It has been recently shown that in going from T to G conformation at a given site the local geometry relaxes into a new energy minimum[8]. Such electronic rearrangement modifies the properties of the C-H bonds, namely from T to G C-H bond distance shortens and the bond stiffens (hence C-H stretching frequency increases[8,9],the equilibrium atomic charge on the H atom increases (hence its intensity decreases)[10] etc. Such changes become an extremely useful and characteristic probe for the identification of G rotamers[11].

Vibrational Intensities. Infrared intensities measure the electronic properties of the molecule at the equilibrium and during the vibrational motion[12].Intensity infrared spectroscopy has been developed in the past few years[12] and is presently being applied also in the case of large molecules. Similarly to what has been done in the past 50 years with force constants parameters which allow to predict frequencies,intensity parameters (EOP, Electro-optical parameters[12]) derived from small molecules allow to predict infrared intensities,i.e. absolute absorption coefficients. In the field of polymethylene chains the concentration of GTG' defects in certain materials(n-alkanes[6],fatty acids ,organic layered perowskytes etc) has been measured through phase transition to melting in order to identify on a molecular basis the mechanism of the transitions.

BAND SHAPES AND BAND WIDTHS

The third piece of information which can be easily obtained from an infrared or Raman spectrometer is the band profile .The theory on band shapes is well established and has been applied to a relatively few cases of small molecules with well resolved and isolated bands. In our study of band shapes for large organic molecules and polymers for which strong overlapping of bands occurs we have measured only band widths which are still a useful physical parameter for the study of the collective dynamics of large organic molecules[13].

The observed band shape in Raman

spectroscopy can be described by the relation:

$$I(\nu) \sim \int dt\, e^{i\nu t} \langle \underline{\underline{\alpha}}(t)\, \underline{\underline{\alpha}}(0) \rangle \qquad (1$$

where the correlation function $\langle \underline{\underline{\alpha}}(t)\, \underline{\underline{\alpha}}(0) \rangle$ is the inverse Fourier transform of the band profile $I(\nu)$. The polarizability tensor can be written as

$$\underline{\underline{\alpha}} = \alpha \underline{\underline{I}} + \underline{\underline{\beta}} \qquad (2$$

where α is the mean polarizability, $\underline{\underline{I}}$ the identity matrix. The first term of eq. (2) is a diagonal tensor or "isotropic term" independent from the orientation of the molecule with respect to a fixed frame.The second term $\underline{\underline{\beta}}$ is a tensor with zero trace called "anisotropic term" which depends on the orientation of the molecule. The scattered light can then be decomposed into an angle independent isotropic and an angle dependent anisotropic component. Raman scattering measurements with suitable polarisation conditions allow to measure independently the two components.If the molecule performs librational or torsional motions about its axis this will appear in the angular dependent anisotropic componenet of the scattered Raman ligth (easily seen in perpendicular polarization geometry).

Parallel geometry brings up the isotropic component related to amplitude dependent terms[13].

Thus the band shape of the anisotropic component contains all the information on the reorientational relaxations of the molecule which is librating or twisting about its main axis;moreover the increase of temperature makes these kinds of motions faster, thus broadending the band width since the vibrational lifetime becomes shorter.The amplitude dependent component is ,instead, practically temperature independent or it may narrow slightly for vibrational dephasing.

THE RAMAN SCATTERING OF POLYMETHYLENE CHAINS IN THE C-H STRETCHING RANGE AS STRUCTURAL PROBE.

It is known that both in infrared and Raman the stretching vibrations of C-H groups appear as strong and sharp bands in the case of polymethylene chains[3]. They have been the subject of innumerous experimental or theoretical studies mainly because strong Fermi resonances take place in this energy range, thus affecting the observed vibrational spectrum.Fermi resonance are particularly dominant in the Raman spectrum of these materials[2,3]

Let d^- and d^+ label the antisymmetric (2890 cm^{-1} ,sharp and strong) and symmetric (2850 $cm,^{-1}$ medium) CH_2 stretching of B_{1g} and A_g species both Raman active. Using the concepts discussed above we expect the band due to d^- to be temperature dependent and give us information on the reorientational relaxation processes of the polymethylene chain, i.e. on the collective librational or twisting motion of the alkyl chain about its main axis.In the case of long alkyl chain or in the case of polymers the end-over-end libration of the molecule is hindered and only the collective tumbling and twisting motion is allowed[13].

Thus the band width of d^- Raman line measures the vibrational lifetime and becomes larger the faster the chain moves about its axis.Since the long alkyl chain is highly flexible like a ribbon while librating can also perform a collective torsional motion about its axis. It can be shown that while band width depends on both kinds of motion, the twisting of the alkyl chain generates selectively also an upward shift of d^- of about 5 cm^{-1} [11]. It is thus possible to distinguish when the molecule librates only or when it also performs a collective torsional motions.

The upward shift of d^- is again related to the changes in the electronic and geometrical properties of the alkyl chain which are clearly and quite sensitively probed by the C-H oscillator.

When the amplitude of the libro-torsional motion becomes too large a conformational kink is generated .Such a kink may remain pinned at the same site of the alkyl chain or may be highly mobile generating a "soliton" like wave. The formation of a conformational kink can be recognized by the appearance of d^- for the distorted structure at frequencies higher of or overlapping with the d^- mode of a alkyl chain in a state of highly cooperative torsional motion.It becomes then possible to follow the phase transitions of systems containing polymethylene chains (hence of liquid crystals and liquid crystal polymers) only from the Raman spectra in the strong, characteristic and isolated range of C-H stretchings.

A similar situation may be revealed by the infrared spectrum of alkyl chains in the C-H stretching range where IR active d^- and d^+ are observed as strong and sharp peaks. However ,the separation of angular and amplitude dependent terms is not possible since the vectorial properties of the dipole transition moment do not allow for such separation which is possible for the Raman tensor.One of the advantages of the infrared spectra is that they are almost free from Fermi resonances which complicate the interpretation of the Raman spectrum.

THE FOURIER TRANSFORM RAMAN SPECTRA OF LIQUID CRYSTAL POLYMERS.

The methods outline above have been used for the study of phase transitions in several systems for which Raman spectra could be easily obtained.

Liquid crystal polymers have been only recently studied using the above concepts, but most of the information were derived from the infrared spectra since Raman spectra could not be recorded since these compounds are highly fluorescent when illuminated with common laser light in the visible range.

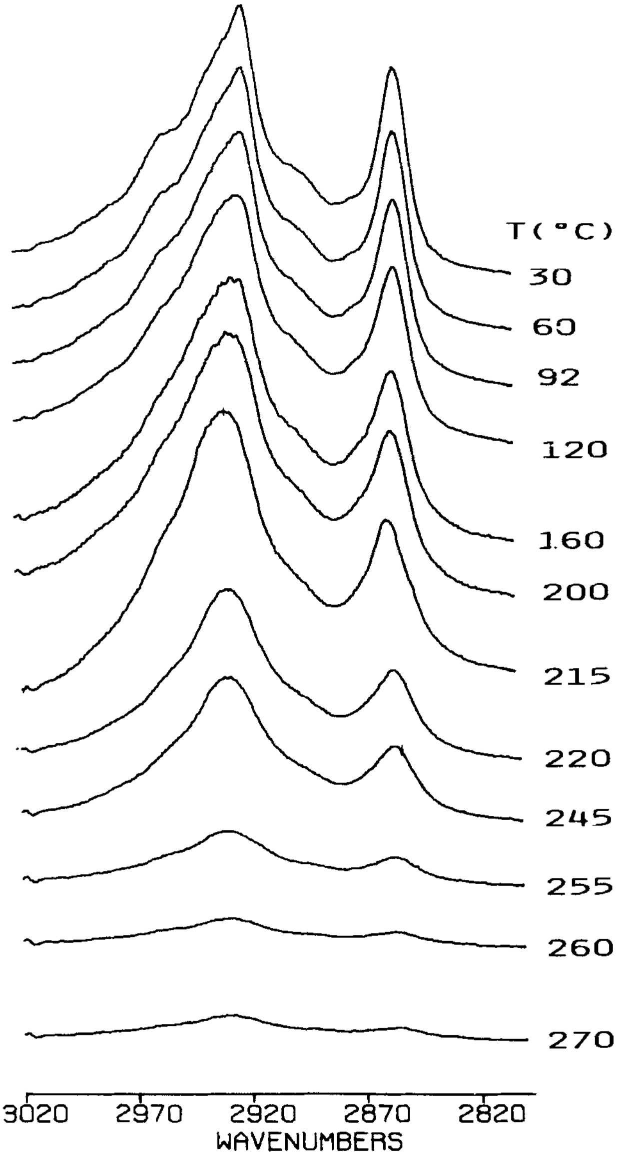

FIGURE 2. Temperature dependent infrared spectrum of the liquid crystal polyester of eq.3

In fig. 2 we report the infrared spectrum as function of temperature for the polyester

$$-\left[-(CH_2)_{10}-O-OC-C_6H_4-O-CO-C_6H_4-CO-O-C_6H_4-CO-O-\right]_n- \quad (3$$

with transitions: K-S =221°C and S-I 260 °C. We do not deal here with the details of the analysis,but only show the overall results. From fig.2 it is clear that the infrared d^- mode of the trans chain dominates and evolves with temperature towards higher frequencies with increasing of the conformational mobility at the K-S transition.

A great step forward the study of liquid crystal polymer comes at present from the possibility of obtaining Raman spectra using a laser light in the infrared.The scattered light is collected and analyzed by Fourier Transform interferometers.

For sake of information in fig. 3 we report for the first time FT Raman spectrum of the same compound as above. The Raman spectrum is consistent with the theoretical concepts described in this article. We believe that the availability of FT Raman spectroscopy will open a very interesting new future to the structural characterisation of liquid crystal polymers.

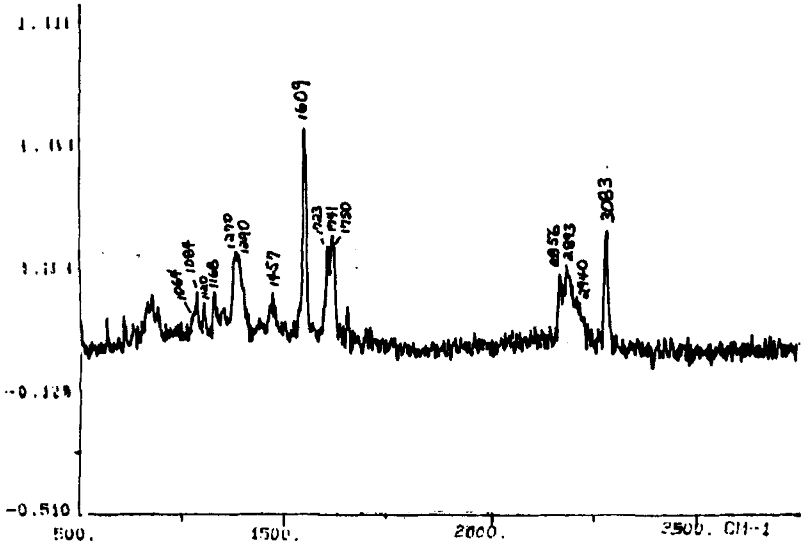

FIGURE 3. FT Raman spectrum of the polyester in eq.2.

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