Study of Micro-Environmental Changes in Liquid Crystalline Compounds Employing Positron Annihilation Technique

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Abstract

For almost last five decades positrons are being used as a nuclear probe to investigate the matter. Positrons obtained from the radioactive decay of neutron deficient nuclide are used as a probe to investigate the matter. On entering into the medium they loss almost all their energy in collisions with the atoms and molecules of the surrounding medium. The thermalised positrons then eventually annihilate with electrons belonging to the medium. Thus the state of the electrons of the medium, in fact, determines the characteristics of positron annihilation process. Positron annihilation technique (PAT) has already been used in the study of water, ice, wood etc. The changes occurring in chemical compounds due to certain reasons have also been studied using PAT. The PAT is also found sensitive towards the structural changes taking place in biological systems. Positron annihilation parameters exhibit their sensitivity toward the structure of DNA.

Positron can, therefore, serve as powerful non-destructive probe to provide useful information about the nature of the environment in which it annihilates. Positron annihilation technique (PAT), in its application, cuts across many interdisciplinary areas like physics, astrophysics, material science, chemistry, biochemistry, biophysics, biotechnology, physical metallurgy etc. It also presents an interesting application in medical diagnostics in the form of positron emission tomography (PET). The possibility of using antimatter (like positron) fuel in spacecrafts is the topic of discussion these days among scientific communities.

In the present study the PAT is used to investigate the liquid crystalline materials n-p-cyano-p-hexyloxybiphenyl (M18) and n-p-
ethoxybenzylidine-p-butylaniline (EBBA). The positron lifetime measurements were taken as a function of temperature in two liquid crystal forming compound. The positron annihilation parameters are found to be very sensitive towards the various modes of molecular motions taking place in these two samples. The results obtained from positron lifetime measurements in the two compounds agree well with existing IR, FIR and Raman spectroscopic studies. Thus we have used this technique as a spectroscopic tool in the study of matter.

Present investigation reveals the excellent potentiality and sensitivity of positron annihilation parameters towards the various kinds of complex molecular motions in the molecules of the M18 and EBBA.

**Keywords:** Positron lifetime | liquid crystals | molecular motions | M18 | EBBA

**Introduction**

The EBBA and M18 are members of liquid crystal forming compounds. Liquid crystals are fascinating materials for studying theoretically and experimentally the characteristics of phase transformations near room temperature. With the increasing use of liquid crystal display devices they have become important materials for the investigation. Positron annihilation parameters have been demonstrated to be extremely sensitive towards the structural and micro-environmental changes taking place in liquid crystalline materials. A compilation of the work has been done by P.C. Jain.

A large class of liquids and liquid crystalline materials can be super cooled far below the crystallization temperature. Below the glass transition temperature, generally, all the molecular motions are supposed to be frozen. However, if the free volume is available some of the molecular motions may still be executed. Such a possibility has been demonstrated in several systems. These investigations have provided useful information about various intra- and inter- molecular modes executed by the molecules. Molecular motions in liquid crystalline materials have been widely investigated using conventional techniques like Infrared and Raman spectroscopy. These techniques have also been employed to elucidate the molecular structure and the nature of intermolecular interaction in such materials.

Recently positron lifetime spectroscopy (PLS) has also been used to study molecular motions in liquid crystal forming materials. In the present study PLS is used to study the super cooled state of EBBA and M18. The present work describes the usefulness of the positron annihilation technique in the investigation of various segmental motions of liquid crystalline molecules.

**Experimental**

In the present study the liquid crystalline EBBA and M18 are used. These were procured from BDH chemicals and were of high purity grade. The transition temperatures from crystalline solid to liquid crystalline state and from liquid crystalline state to isotropic state, as observed in the present study, agree well with those reported in literature. It was, therefore, used without any further purification. EBBA has a molecular weight of 281 and negative dielectric anisotropy in the nematic phase. Its molecule has a dipole
moment ~2.19 Debye. When heated from a crystalline phase it first changes to nematic mesophase and then to isotropic phase. The transition temperatures are shown below

\[
\text{Crystalline Solid} \rightarrow 309\, K \rightarrow \text{Nematic} \rightarrow 351\, K \rightarrow \text{Isotropic}
\]

It has the following molecular structure

![Molecular Structure](image1)

Fig.1: Molecular Structure of Ethoxybenzylidene Butylaniline (EBBA)

M18 has a molecular weight of 279 and negative dielectric anisotropy in the nematic phase. Its molecule has a dipole moment ~4.5 debye. When heated from a crystalline phase, it first changes to nematic mesophase and then to isotropic phase. The transition temperatures are shown below

\[
\text{Crystalline Solid} \rightarrow 330\, K \rightarrow \text{Nematic} \rightarrow 348.5\, K \rightarrow \text{Isotropic}
\]

It has the following molecular structure

![Molecular Structure](image2)

Fig.2: Molecular Structure of hexyloxy cyanobiphenyl (M18)

A standard positron lifetime spectrometer is used for the measurement of positron lifetime. The radioactive positron source used was $^{22}\text{Na}$. It was prepared by evaporating a few drops of aqueous solution of $^{22}\text{NaCl}$ on a thin Mylar film (~10μg cm$^{-2}$). It was then covered with another similar film. The source sandwich was sealed by putting it in between two concentric tightly fitting stainless steel rings. It was then placed in the sample contained in a cylindrical glass ampoule. The Mylar film thickness used was such that less than 5% of the positrons were annihilated in it. Appropriate correction for these annihilations was applied when analyzing the data. The ring diameter and the source positions were such that no positrons annihilated in the ring. The sample temperature was slowly increased till the isotropic phase was reached. The sample was kept in this state for a long enough time so as to wipe out any previous thermal history. It was then cooled slowly till the sample was in liquid crystalline state. It was held in this state for ~ 30 minutes and then quenched by dropping the copper ampoule, containing the sample, directly into liquid nitrogen. The quenching state achieved in this process was better than ~ 10 Ks$^{-1}$. The temperature of the sample was maintained thermostatically at each step to a constancy of ±0.1°C. In each set of measurement a total of $2\times10^5$ counts were collected.

In the present investigation two sets of positron lifetime measurements were performed; one during the heating cycle of the samples prepared by quenching and second during the heating cycle of the samples prepared by slow cooling (cooling rate ~ 1K/min) from the liquid crystalline phase down to about 150K.

**Results and Discussion**
The lifetime spectra recorded in the present work were analyzed using the software PC-PATFIT, developed by Riso-National Laboratory, Denmark\textsuperscript{10}. All the lifetime spectra could be resolved into three components. The shortest component, $\tau_1$, was constrained to 0.125 ns, the parapositronium (p-Ps) lifetime. Parapositronium is a singlet bound state of electron and positron having antiparallel spins. The intermediate component, $\tau_2$, has been attributed to the annihilation of positrons with electrons of the medium without forming a bound state. It is usually referred as free annihilation. This component was found to be insensitive to any structural change occurring in the medium. The longest component, $\tau_3$, is ascribed to the pick-off annihilation of ortho-positronium (o-Ps) with electrons bound to the molecules of the surrounding medium. The o-Ps is a triplet state having parallel spins of electron and positron. $\tau_3$ exhibits considerable temperature dependence and sensitivity to structural changes occurring in the medium. The relative intensity $I_3$ of this component is, therefore, proportional to Ps formation in the medium.

The temperature dependence of the positron annihilation parameter $\tau_3$, in the present investigation, for EBBA is shown in figure 3. This Figure depicts the temperature dependence of $\tau_3$ in quenched and slow cooled samples.

As seen from figure 3 for the slow-cooled sample (open circles), the gradual increase in the value of $\tau_3$, in the temperature range 165 to 300 K, is commensurate with the thermal expansion of the crystalline solid. The transition from crystal to crystal lattice. Which again indicate that on slow cooling the material transforms simply to a nematic and nematic to isotropic phase are indicated respectively at 309 and 351 K. These transition temperatures agree with the literature reported values. The temperature dependence of $\tau_3$ for the quenched sample (filled circles), as seen from fig.3, is quite different from that exhibited by the slow cooled sample. For the quenched sample, the $\tau_3$ plot exhibits eight distinct peaks at 172, 178, 186, 196, 205, 222, 230 and 241K respectively. The transition seen at ~255K is typically a glass transition\textsuperscript{14}. In a glass transition region, the system exhibits relaxation behavior. The plots of $\tau_3$ for the quenched and slow cooled samples merge at ~290 K.

EBBA is a large asymmetric molecule having a C$_3$H$_7$O- group attached at one end and C$_4$H$_9$- group at other end. The –HCN- group lies in between the two phenyl rings. In the liquid crystalline phase, the system exhibits a partial order, namely the long range orientational order. Because of these special features, this class of materials executes various intra- and inter-

![Fig.3: Temperature dependence of $\tau_3$ in EBBA:](image-url)
molecular motions. Exclusive work to study such motions has been done in various systems using FIR and positron lifetime spectroscopy. In the present study, as the quenched sample is gradually heated, various modes get excited at temperatures corresponding to their characteristic frequencies. Since the associated relaxation times of the system in the super cooled state are quite large compared with the o-Ps pick-off lifetimes in the systems, the annihilating o-Ps atoms localized in the voids may pick up the motions executed by the molecules. Such a possibility is reflected in the form of various peaks in the plot of $\tau_3$ for the quenched sample. The shape of the peaks can perhaps be understood in terms of the response of the system. As the temperature corresponding to a particular mode is approached, the molecules execute a greater response. It becomes maximum when the temperature coincides with that corresponding to a particular mode. The system thus exhibits a kind of resonance behavior. The high viscosity of the system affects the sharpness of the resonance. With increasing amplitude of the molecular motion, the size of the voids, which act as efficient traps for Ps, also increases and hence the o-Ps pick-off lifetime $\tau_3$. Thus the temperatures at which the peaks occur in the $\tau_3$ plot for the quenched sample correspond to characteristic frequencies of different motions of the molecules. The temperatures of the various peaks observed and the wave numbers of the corresponding probable molecular motions are given in table 1.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Wave Number (Cm$^{-1}$)</th>
<th>Tentative Assignments of the Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>172</td>
<td>120</td>
<td>Libration motion of benzene ring</td>
</tr>
<tr>
<td>178</td>
<td>124</td>
<td>Libration motion of benzene ring</td>
</tr>
<tr>
<td>186</td>
<td>130</td>
<td>Libration motion of benzene ring</td>
</tr>
<tr>
<td>196</td>
<td>136</td>
<td>Libration motion of benzene ring</td>
</tr>
<tr>
<td>205</td>
<td>143</td>
<td>Torsional motion of the molecule about long axis</td>
</tr>
<tr>
<td>222</td>
<td>155</td>
<td>Collective mode</td>
</tr>
<tr>
<td>230</td>
<td>160</td>
<td>-HCN- torsional motion</td>
</tr>
<tr>
<td>241</td>
<td>168</td>
<td>Collective mode</td>
</tr>
</tbody>
</table>

Table1: Molecular modes of EBBA molecules as observed in the present work

The modes observed at 120, 124, 130 and 136 cm$^{-1}$ might be attributed to the twisting motion of the benzene rings with respect to their own principal axes. In the FIR studies of MBBA (a lower homologue of EBBA) by Sciesinsks et al$^{15}$ the bands observed at 94, 102, 117 and 137 cm$^{-1}$ were interpreted as due to liberational modes of benzene rings with respect to an in-plane axis and six fold axis. According to Gruger and Calve$^{18}$ the vibrational mode at 100 cm$^{-1}$
observed in aromatic compounds has its origin in the librations of the benzene rings. The presence of the –HCN- group between the phenyl rings in EBBA weakens the linkage between them and thus makes it possible for these benzene rings to execute independent libration motion with respect to their own principle axes.

The peak observed at 143 cm$^{-1}$ in the present investigation may be attributed to the torsional motion of the whole molecule about the long molecular axis. In the FIR study of MBBA Evans et al$^{19}$ have applied Brot molecular dynamics model and interpreted the 130 cm$^{-1}$ mode as arising from the whole molecule librations about the long molecular axis. Such a band was also observed in Raman$^{20}$ and infrared$^{16}$ spectrum of MBBA. Since the added alkyl chain in EBBA as compared with MBBA, practically lies along the long molecular axis, the related change in moment of inertia of the molecule about its long axis is negligible. Therefore the torsional motion of whole molecule about the long molecular axis is expected to occur almost at the same characteristic frequency in both EBBA and MBBA. A slightly higher value of frequency in the present investigation as compared with the existing results of the other conventional techniques may be due to the different environments to which the molecules are subjected. In our case the molecules encounter high viscosity; the molecular motion is more sterically hindered.

In the FIR study of K21$^{3,5}$ two molecular modes obtained respectively at 150 and 175 cm$^{-1}$ were explained as due to the collective motion of the molecule. EBBA used in the present investigation exhibit nematic mesophase when heated from their crystalline state. The nematic liquid crystal is characterized by the tendency of molecules to lie with their long axes parallel even when large distances separate them. Such a long range orientational order offers a situation in which group of molecules can give rise to collective modes. Since the system in the present study is quenched from the nematic phase, picking of these collective modes are possible even in the glassy phase where the nematic characteristics still exist. In the positron annihilation studies of K21 and K30$^{9}$ the modes at 149 and 172 cm$^{-1}$ were ascribed to these motions. The observation of collective modes almost at the same frequencies for the two compounds perhaps indicates that the molecular structure rather than the molecular weight plays more dominant role in controlling the nature of long range order of the liquid crystal and hence the collective motion of the molecules. Thus due to different structures, the collective modes in EBBA may arise at different characteristic frequencies as compared with those of K21 and K30. In this context, the wave numbers 155 and 168 cm$^{-1}$ may correspond to the collective mode of EBBA molecule. In the present study the mode associated with the wave number 160 cm$^{-1}$ may be assigned to the torsional mode of –HCN-group.

Positron annihilation lifetime studies carried out in M18 have also yielded similar results. In this case the quenched sample exhibits six broad peaks at -100, -81, -60, -43, -23, -18 °C. A glass transition and transformation from solid to nematic phase are observed at -11 and 57 °C.
respectively. Similar to EBBA the broad peaks observed here are attributed to segmental motions of M18 molecules occurring at 120, 134, 148, 160, 174 178 cm\(^{-1}\) respectively.

**Conclusion**

The present study shows that molecular motions are possible even below the glass transition temperature and positron annihilation parameters are found to be sensitive to various intra- and inter-molecular modes executed by the molecules. The frequencies of some of the modes observed in the present work agree with the literature reported values obtained from FIR and Raman studies. For others only tentative assignments have been made. The present investigation thus demonstrates that positron lifetime spectroscopy can be used for studying various molecular motions.

**References**
