



Ortho-Positronium Lifetime and Formation Probability Variation Outcomes in Liquid Crystalline Decyloxy Cyanobiphenyl

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ABSTRACT

Decyloxy cyanobiphenyl is one of the homologues of alkyloxy cyanobiphenyl series. It is represented as 10OCB or M30. Positron lifetime measurements have been carried out both in the heating and cooling cycles of the sample. Positron lifetime parameters were found to be sensitive in detecting solid to liquid crystalline and liquid crystalline to isotropic phase transitions. Variation in ortho-positronium lifetime magnitude suggests some special structural changes occurring in the sample. These structural changes include solid K₁ to solid K₂ transformation at 35^oC, solid K₂ to solid K₃ transformation at 55^oC, solid to liquid crystalline transformation at 59^oC, liquid crystalline to liquid phase transition at 84^oC, retention of some memory of more ordered crystalline state in liquid crystalline phase and antiparallel bimolecular pairing. These transition temperatures agree well with those reported in literature for this compound. The ortho-positronium formation probability I₃ shows a remarkable change as we compare its values in other homologues of this series. This is described in detail in 'Observation and Their Outcomes'.

Keywords: Decyloxy Cyanobiphenyl, O-Ps Lifetime, Solid Crystalline Polymorphism, Phase Transformation

Introduction

Positrons emitted by radioactive source, on entering into material media, lose almost all their energy in ionic collisions. The thermalized positrons, then eventually annihilate with the electrons of the media. The lifetime of positron is therefore, governed with the state of electron in the media with which it annihilates. That is why the positron lifetime varies with the structural changes taking place in the system under investigation.

The liquid crystals are sometimes known as fourth state of matter. They are fascinating state of materials and are used in liquid crystal displays. M30 is a liquid crystal forming compound having very large dipole moment associated with its nitrile bond. Due to this large dipole moment associated, they arrange themselves anti parallel to each other and form a kind of bimolecular association [1-3]. The apparent length of this anti-parallel pair in the liquid crystalline phase is found to be greater than the actual molecular length. As per the

dielectric study performed in this compound, it has been shown that the extent of antiparallel pairing decreases as one approaches isotropic liquid phase [4]. Some of the members of this series exhibit layered smectic phase, characterized with interdigitated semi-bilayer structure. If on heating such a smectic phase, a nematic phase is obtained, then small aggregates of this interdigitated structure persists even in nematic phase [1, 2]. These small aggregates of molecules are known as cybotactic clusters. The size of these clusters decreases with increasing temperature [5]. Another interesting feature reported to be associated with cyanobiphenyl liquid crystalline materials is the solid crystalline polymorphism [6-8].

In present investigation, various characteristics and micro-structural changes taking place in liquid crystalline material M30, were picked up by positron annihilation parameters. A compilation of this work has been done by P.C. Jain [9]. A study of complex molecular motions in alkyl- and alkyloxy- cyanobiphenyls was performed by M. Sharma and K.C. Singh, employing positron lifetime spectroscopy [10-13]. The present work demonstrates the effectiveness and sensitivity of positron annihilation parameters in detecting various characteristic features of M30. Initial efforts, in investigating various characteristics of this kind of compounds were made by Malhotra et al [14, 15] and Jain et al [16]. In Present investigation, a systematic temperature-dependent positron lifetime measurements were performed on M30.

Materials Used

The positron source used in present study was ^{22}Na . The decay scheme of this source is shown in figure 1. The radioactive sources, with neutron deficient nuclei, are generally used as positron sources. In this kind of nuclei, a proton is converted into a neutron by emitting a positron. There is almost a simultaneous emission of 1.276 MeV gamma radiation with the birth of positron. Thus, this 1.276 MeV gamma energy radiation provides the birth signal of positron. The positron annihilates with electron of the medium by emitting a 0.511 MeV gamma ray. A correlation between 1.276 and 0.511 MeV radiations, thus, gives an estimate of positron lifetime in the medium.

The positron source was prepared by evaporating a few drops of aqueous solution of $^{22}\text{NaCl}$ on a thin mylar film and then covering it with another similar film. The source sandwich was sealed by putting it in between two smooth, concentric, tightly fitting stainless steel rings. It was then fixed in the grooves of a specially designed glass container and then this container was sealed properly. The temperature of the sample was thermostatically maintained constant in every cycle of measurement. In each set of measurement a total of two lakh counts were collected. The liquid crystalline material used in the present study, M30, was procured from British Drug House Chemicals, UK. It was of high purity grade, therefore, used without any further purification.

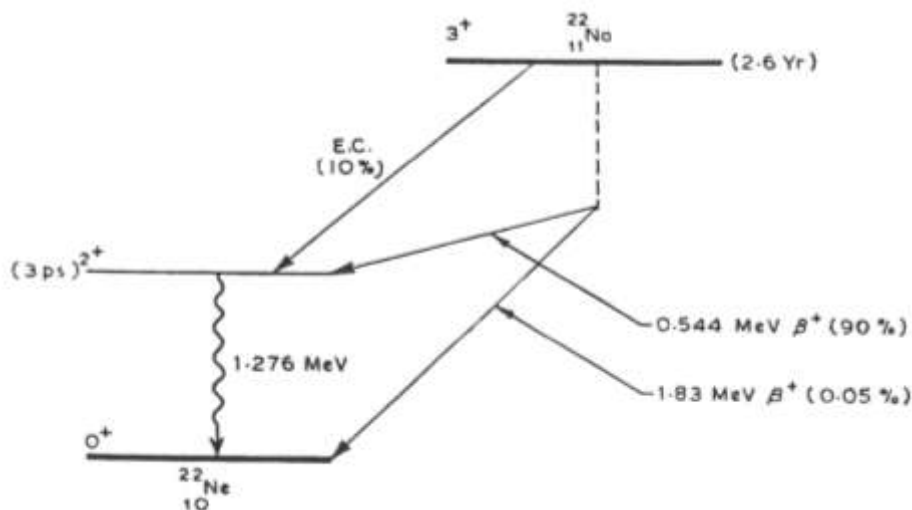


Figure1. Decay Scheme of Positron Source ^{22}Na

Positron Annihilation Parameters

Positrons emitted by radioactive source annihilate via three processes; free annihilation, self-annihilation and pick-off annihilation. The annihilation of positron with free electrons of the system under investigation is known as free annihilation. Free annihilation lifetime and its relative intensity are represented by τ_2 and I_2 respectively. The bound state of positron is very much similar to hydrogen atom with proton replaced by positron. It is known as positronium. Positronium may exist in two states either para-positronium (p-Ps) or ortho-positronium (o-Ps). The annihilation of positron, with the electron with which it is bound, is known as self-annihilation. The self-annihilation lifetime of para-positronium is 0.125 ns and that of ortho-positronium is 140 ns. The p-Ps lifetime and its intensity of formation are represented by τ_1 and I_1 respectively. Due to its long lifetime, instead of self-annihilation, o-Ps generally picks up an electron from surrounding medium and annihilates with it. This is known as pick-off annihilation. The pick-off annihilation lifetime of o-Ps and its intensity of formation are represented as τ_3 and I_3 respectively. Both these parameters exhibit considerable temperature dependence and sensitivity to structural changes occurring in the medium.

Observations and Their Outcomes

A systematic temperature dependent measurement of parameter I_3 , as a function of number of carbon atoms in the alkyl chain, is shown in figure 2. In the four homologues of alkyloxy cyanobiphenyl series, i.e., in 6OCB, 8OCB, 9OCB and 10OCB, the number of carbon atoms are 6, 8, 9 and 10 respectively. The parameter I_3 exhibits some interesting trends not shown by τ_3 . As shown in figure 2, in the solid phase, a systematic decrease in its value is observed as one goes from a lower homologue to a higher homologue. However, in the mesophase no such trend is observed. It is seen from the figure that in 6OCB the I_3 values in the solid phase are higher as compared to those in liquid crystalline phase, whereas a reverse trend is observed in other compounds. Normally, due to compactness of the system a lower positronium formation (proportional to I_3) is expected in solid phase compared with liquid crystalline phase as has been observed in three homologues 8OCB, 9OCB and 10OCB. However, this does not seem to apply to 6OCB for which solid phase appears to be more favourable to positronium formation as compared with liquid crystalline phase. Figure 2 reveals that there appears to be a gradual transformation in the nature of molecular packing in solid crystalline phase as we go from a lower to higher homologue. The solid in 6OCB appears to possess a more open packed structure than the solid in 10OCB. The length of the alkyl chain seems to influence the packing character of the molecules.

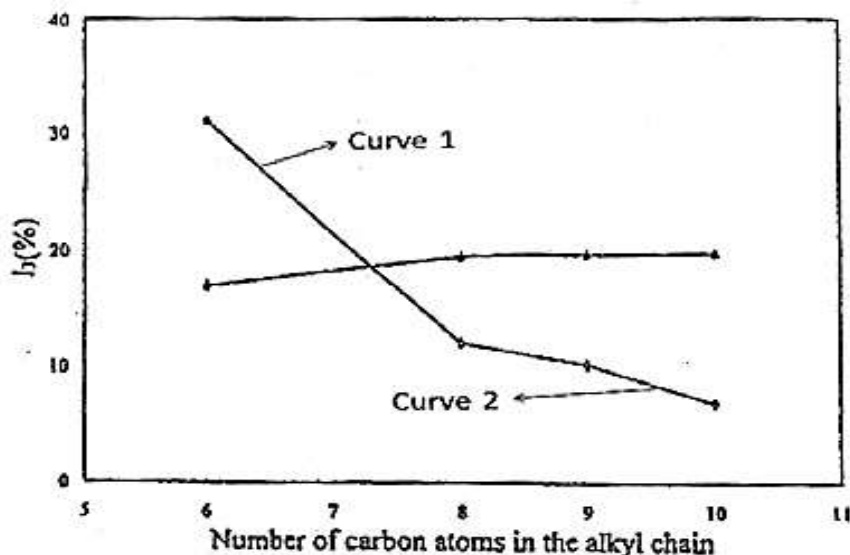


Figure 2. Variation of I_3 with the number of carbon atoms in the alkyl chain; curve 1 represents solid phase and curve 2 represents liquid crystalline phase.

It is mentioned previously that the positronium formation probability is represented by I_3 . Figure 3 represents the temperature dependence of I_3 in the compound investigated. This parameter is not as sensitive as ortho-positronium lifetime τ_3 , in detecting solid crystalline polymorphism and formation of cybotactic groups. Normally due to the compactness of the structure, a lower positronium formation is expected in solid phase as compared to liquid crystalline phase. The same trend is obtained in the compound investigated.

Variation in o-Ps pick-off lifetime τ_3 with temperature, in liquid crystalline M30, is shown in Figure 4. Positron lifetime parameters picked up, some of the important features like solid crystalline polymorphism, retention of memory of crystalline state even in passing to liquid crystalline phase, formation of cybotactic groups and relaxational behavior. Positron annihilation lifetime spectroscopy was used to investigate solid crystalline polymorphism in various liquid crystalline materials [6-8]. Present study provides evidence for the existence of solid crystalline polymorphism in M30. It is shown that Solid K_1 to Solid K_2 transformation takes place at temperature 35°C and solid K_2 to Solid K_3 transformation takes place at 54°C . These transformations are represented by arrows on temperature axis in figure 4. Solid crystalline polymorphism, in similar liquid crystalline material octyloxy cyanobiphenyl, has also been reported using Raman spectroscopy [7], ac calorimetry and picosecond time resolved fluorescence [17], and DSC, X-ray diffraction and optical microscopy [18].

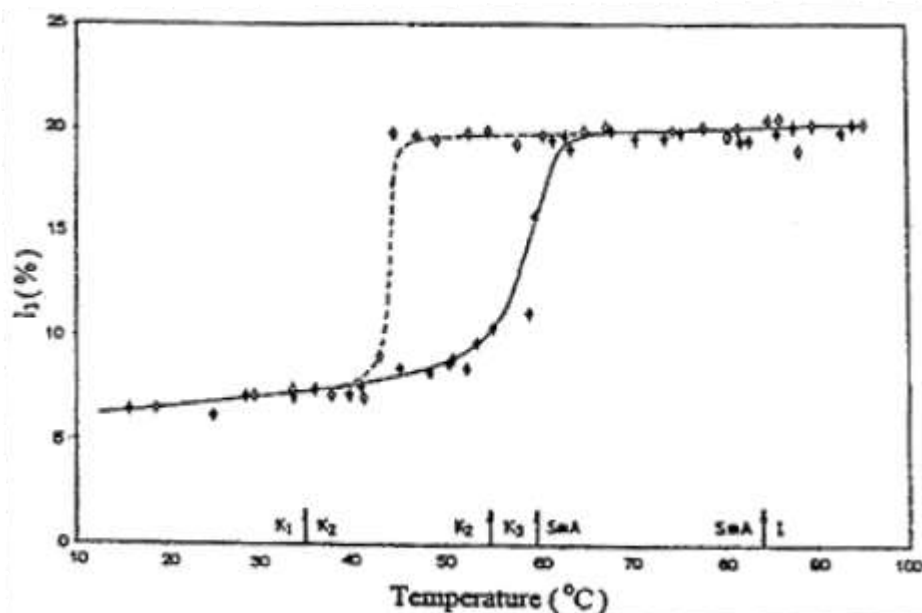


Figure 3. Temperature dependence of I_3 in M30. Solid circles represent the heating cycle and hollow circles represent cooling cycle..

At 54^oC, τ_3 begin to increase gradually indicating the growth of a new structure. This gradual increase in τ_3 value, in temperature range 54 to 80 ^oC, is indicating two possibilities. Either a new crystalline phase K_3 begins to grow at the expense of K_2 phase or growth of liquid crystalline SmA phase which is inter-dispersed in K_2 . The first possibility supports the metastable character of K_2 phase. The continuously increasing value of τ_3 over this temperature range supports the metastable character of K_2 phase. As the temperature is raised the content of SmA increases at the expense of K_3 phase. At 60^oC, the SmA content reaches a critical limit and the system completely transforms to SmA phase. At 85^oC, system again transforms its state from smectic to nematic.

In the investigated compound M30, the observed change in τ_3 at solid to liquid crystalline phase transition does not commensurate with the corresponding change in free volume. In present study, the change in τ_3 value at solid to liquid crystalline phase transition is approximately 70%, whereas the corresponding change in its density is reported to be 5-10%. Such a large change in τ_3 can be attributed to the phenomenon of anti-parallel molecular pairing. This kind of pairing is reported in literature by similar compounds [1-3]. This bimolecular association occurs as a result of interaction between the dipoles induced by powerful electron withdrawing cyano groups and the easily polarizable phenyl groups. In the smectic phase, intermolecular attractive forces relax due to increased thermal energy and the large overlapping is achieved. This can be achieved only by a shift of the molecules with respect to each other along the crystal axis. The transition, thus, is of displacive type [19]. Such an anti-parallel pairing in liquid crystalline state, leads to scarce availability of free dipolar endings, probable sites for o-Ps pick off to take place. This lowering of ortho-positronium pick off rate increases τ_3 value in liquid crystalline phase. A small decrease in τ_3 value at liquid crystalline to isotropic liquid state transition could also be attributed to a decrease in the extent of anti-parallel pairing as reported in dielectric studies [4].

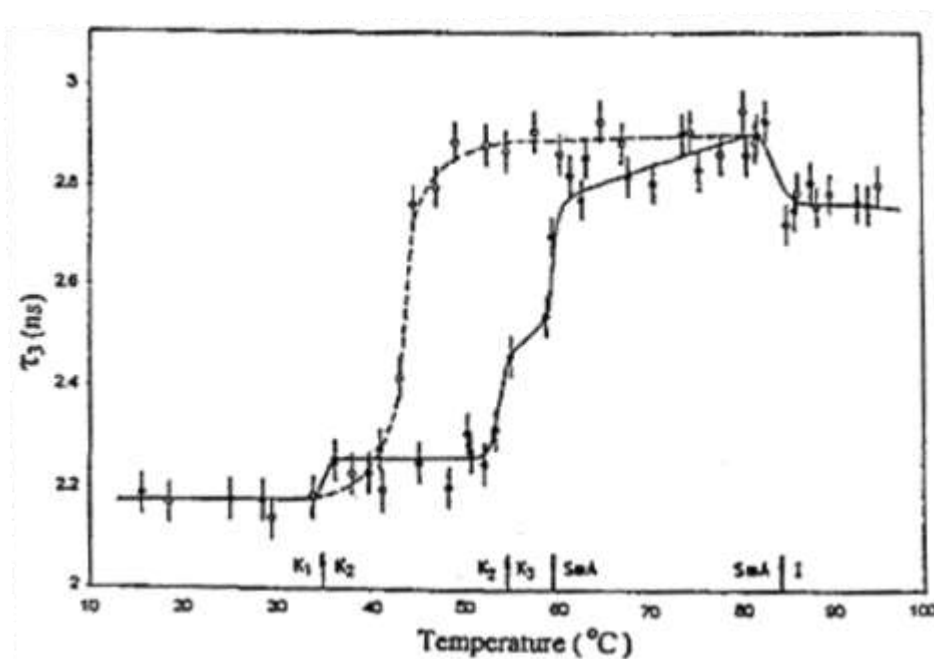


Figure 4. Temperature dependence of τ_3 in M30: The arrows on the temperature axis represent solid crystalline to liquid crystalline and liquid crystalline to isotropic liquid transitions.

Ortho-positronium lifetime τ_3 is found to increase gradually with increasing temperature in liquid crystalline state adjacent to crystalline solid state. In this region, the rate of increase of τ_3 is not in keeping with the thermal expansion of the system. This behavior could be attributed to retention of some memory of higher ordered crystalline phase and its gradual disappearance as the temperature in this region is increased. This view is supported by the results obtained during cooling cycle. During the cooling cycle, in the liquid crystalline phase, τ_3 maintain a near constant level instead of retracing the plot obtained in heating cycle. During the cooling from isotropic liquid phase, the material passes from a less ordered state to higher degree ordered liquid crystalline phase and therefore, there is no constraint of any memory of previous phase.

Conclusions

It is found that positron annihilation lifetime (o-Ps lifetime) is not only sensitive enough in detecting gross features like phase transformations but also to micro structural changes occurring in the liquid crystal forming M30. The positron annihilation lifetime shows considerable variations for phenomena like solid crystalline polymorphism, anti-parallel bimolecular pairing, and retention of solid crystal order in liquid crystalline phase. It is observed that τ_3 is more sensitive parameter than I_3 , in its response to various characteristic changes occurring in the system. Although, the value of I_3 remains almost constant throughout the K_2 solid phase but increases gradually with increasing temperature in K_3 phase. This reveals the fact that system transforms from a closely packed to open pack structure and finally transforms to liquid crystalline phase. Thus the peculiar behavior of I_3 in the solid phase of M30 indicates a kind of molecular repacking.

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