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Electron momentum distribution mapping of *trans*-stilbene single crystal by positron annihilation

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Abstract

Two-dimensional electron momentum distributions mapping in a molecular *trans*-stilbene crystal has been done, first time using two-dimensional angular correlation of positron annihilation radiation. The measured coincident annihilation spectra for the plane corresponding to *c*–*a*, projected to crystallographic *b* direction have been elucidated.

1. Introduction

Positron annihilation as non-destructive probe has been used extensively to investigate the electron momentum distribution (EMD) in metals, intermetallics and organic and inorganic molecular crystals and on semiconductors [1,2]. This technique is well suited for the study of the local electronic environment probed by the positrons in solids and for characterisation of defects at the atomic scale. Many researchers have used positrons to investigate the electronic structures by mapping the EMD from the annihilated anticollinear photons carrying information of the electron momentum proportional to the electron density [1–3]. The interest on the study of organic molecular crystals is to understand the positron behaviour in the molecular crystals owing to their chemical environment and physical structure.

trans-Stilbene, one of the most useful organic crystal scintillators has very flexible molecules in the ground state with high scintillation efficiency and a short decay time. This crystal belongs to the monoclinic space group $P2_1/c$ with four molecules in the unit cell [4–9]. An interesting feature of this molecular crystal is the high structural disorder at room temperature with one of the two independent sites showing orientational disorder [4–9]. The candidate is also noted for its interesting electronic structure and liquid crystal features at room temperature. The luminescence in organic crystal scintillators generally depends on the local electronic environment. The efficiency in luminescence is associated with conjugated and aromatic organic molecules arising from their π-electronic structure [10–16]. Such molecules form organic molecular crystals by means of a weak force called van der Waals force and retain their individual identity, and their electronic structure. Studies on electronic structure from EMD in *trans*-stilbene by positron annihilation technique seem to have been unpublished so far.

Earlier X-ray studies on *trans*-stilbene have revealed the highly disordered structure at room temperature and perfectly ordered at low temperature [4–8]. Quasi continuous phase transition and a second order phase

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transition on the basis of luminescence technique were reported based on Raman spectroscopic studies [17]. Positron lifetime measurements by Bokor et al. [18], the only report on this material, have revealed a high intense short lived component and hardly a long lived positron lifetime component. These were attributed to the annihilation with the delocalised electrons and the hindrance of positronium formation due to its aromatic structure at room temperature [18]. Further these studies also revealed the phase transition at low temperature and a meager probability of positronium formation. DSC measurements on these materials also exhibited the spreading of phase transition over a wide temperature range [18]. These investigations revealed the orderliness and disorderliness in its lattice structure at lower and higher temperatures, respectively.

In this Letter, we report the mapped two-dimensional EMD on *trans*-stilbene. The mapping was carried out using the two-dimensional angular correlation of positron annihilation radiation (2D-ACAR) to understand the electronic structure [1]. We present our investigations on the study of the static and dynamic electron distribution by positron annihilation and the positron behaviour in this material. The present measurements will serve as a prelude to the 2D-ACAR studies on phase transition and characterisation of defects. To the best of our knowledge, the present EMD study is the first report on the aromatic molecular crystals.

2. Experiment

In this technique, upon entering the solid, positrons get thermalised and annihilate with the electrons resulting in two anticollinear (180°) gamma photons. Small angular deviation from its anticollinearity gives information of the electron momentum resulting from the annihilation. Mapping of these angular deviations by a pair of large area position sensitive detectors (PSD) operating in coincidence exhibits the EMD $N(p_x,p_y)$ [1–3]. The measured 2D-ACAR spectrum is proportional to the two-dimensional projection of the momentum density $\rho^{2\gamma}(\boldsymbol{p})$ of the electron–positron pair along a selected axis p_z. That is,

$$N(p_x,p_y) \propto \int \rho^{2\gamma}(\boldsymbol{p})\,\mathrm{d}\boldsymbol{p}_z. \tag{1}$$

The resulting distribution provides the electronic structure and the symmetry of the projected plane of interest.

Obtaining good quality molecular single crystal in a given run is always a probability and the formation starts only after the initiation of the seed [21]. Crystals for this present study have been grown with various efforts like zone purification of the starting material, alteration of growth vessel shape, varying the temperature gradient and by adopting suitable growth rates (ampoule lowering rate). The effects of all these parameters on the growth of stilbene single crystal have been reported elsewhere [22,23]. Selective self-seeded vertical Bridgman Technique (SSSVBT) has been used for the growth of single crystals with better quality [22–25] and was used for the present study. Polished sample of $7 \times 7 \times 5\ \mathrm{mm}^3$ size was used. The planes of the grown crystal were identified by using Enraf Nonius Single Crystal X-ray Diffractometer. The grown crystals show (0 0 1) cleavage plane. The determined lattice parameters $a = 15.720$ Å, $b = 5.741$ Å, $c = 12.394$ Å and $\beta = 112.096°$ are in good agreement with the previously reported values [4–9]. The sample was mounted in a specially designed holder ≈3 mm away from the ^{22}Na positron source in a lead chamber, such that [0 0 1] direction was along the *X*-axis (facing the positron source) and [1 0 0] along *Y*-axis. The measurements were carried out by the indigenously developed 2D-ACAR system based on position sensitive large area Anger cameras (NaI(Tl) crystal mounted on 37 PMT's) kept at 8.3 m apart from the sample under study [19,20]. The system is operative in coincidence for the 511 keV annihilated photons with a timing resolution of 30 ns. The acquired images are stored as histograms of $N(p_x,p_y)$, after focal plane transformations. Typically the data obtained were in steps of $\sim 0.35 \times 0.35\ \mathrm{mrad}^2$ (bin resolution) and it is the angular resolution. The overall angular range of $45 \times 45\ \mathrm{mrad}^2$ is displayed in the form of a histogram matrix of 128×128 bins. The data were collected for 10 days for a total count of 6×10^6 counts and the experiment was repeated for good statistics and consistency on the observed features. All the measurements were carried out at room temperature. The resulting $N(p_x,p_y)$ corresponds to the EMD of the positron–electron pair integrated along the p_z direction. Prior to analysis, the as collected data were corrected for angular efficiency due to the non-uniform response on the detector surface. Further the distribution was folded to its symmetry according to the crystallographic direction followed by a rough smoothing using a Savitzky-Golay filter and edge correction in order to improve the quality of the images.

3. Results and discussion

Fig. 1a,b displays the surface and contour plots of the EMD projected to [0 1 0] such that p_x along [0 0 1] and p_y along [1 0 0]. The distributions are presented for −11.25 to +11.25 mrad with contour spacing of 1/16 of the maximum value. The iso-surface distribution clearly shows the characteristic EMD with a flat-topped feature. From the contour plot, the distribution in the low momentum region (LMR) upto ±2 mrad along the p_x direction and ±1.6 mrad along the p_y direction is observed to be an ellipse with major and minor axes