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Structural and optical studies on ortho-hydroxy acetophenone azine thin films

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The bulk material and deposited thin films of ortho-hydroxy acetophenone azine (*o*-HAcPhAz) were identified by X-ray diffraction (XRD) to be single phase polycrystalline of the monoclinic structure. The unit cell lattice constants were determined to be $a = 1.578$ nm, $b = 1.394$ nm and $c = 0.64$ nm, as well as its plane angles as $\alpha = 90^\circ$, $\beta = 123.8^\circ$ and $\gamma = 90^\circ$. FTIR spectra of the bulk and thin films of the compound under investigation were assigned in the wave number range 4000–500 cm^{-1}. It was revealed that they were similar to each other. The optical constants (the refractive index, n, and the extinction coefficient, k) of the compound thin films were determined from the measured transmittance, T, and reflectance, R, at normal incidence of light in the spectral range 200–2100 nm. The plot of the absorption coefficient (α) versus $h\nu$, gave three intense bands and a shoulder which were designated as A (232.3 nm), B (299.5 nm) and C (440.6 nm, 404.8 nm, sh). The observed A and B bands were attributed to $\pi\ \pi^*$ transitions, while the C-bands were attributed to $\pi^* \leftarrow \sigma(n)$. The optical high frequency dielectric constant (ε_1, ε_2) as well as the real and imaginary parts of the optical conductivity (σ_1, σ_2) were determined. The plots of both ε_1, ε_2, σ_1 and σ_2 versus $h\nu$ reveal the same obtained optical transitions. Also, the relationships between both of surface, volume and surface/volume energy losses against $h\nu$ gave the same optical transtions.

1. Introduction

Substituted aromatic azines like ortho-hydroxy acetophenone azine (Fig. 1) have shown thermal and photochemical isomeriation about the C=N bands or rotation about the N–N bond [1–4]. They have considerable interest for their lasing properties and useful applications in colouring and dyeing processes [1]. The electron system of compounds such as ortho-hydroxy acetophenone azine (*o*-HAcPhAz) is considered to be delocalized to some extent from which arises the semiconducting properties [5, 6]. In the present work attention was directed to investigate the structure of such compounds as bulk and thin films using XRD and FTIR techniques. The goal of this work was to study the optical properties of the ortho-hydroxy acetophenone azine thin films. To our knowledge, no work concerning the optical properties of *o*-HAcPhAz thin films has been reported.

2. Experimental

2.1. Bulk material synthesis

The ortho-hydroxy acetophenone azine (Fig. 1) was prepared from analar grade (BDH) starting materials in a stoichiometric ratio of 2 : 1 of aromatic aldehyde and hydrazine monohydrate. More details about the preparation were reported by Jain *et al.* [7]. Recrystallization of the obtained compound was carried out in ethanol. Chemical analysis and infrared spectra were established to identify the purity and formation of the compound.

2.2. Thin films preparation

Thin films with different thicknesses were prepared, by the deposition of the bulk material onto precleaned quartz and glass substrates held at room temperature during the deposition process, by thermal evaporation at controlled conditions, using a high vacuum coating unit (Edwards E 306A). In the thermal evaporation technique with a single source, the evaporator (molybdenum boat) was charged with ortho-hydroxy acetophenone azine in granulated form. Well-cleaned quartz and glass substrates were clamped to a suitable holder and the vacuum chamber was then pumped down to 10^{-5} Torr. In the initial stage of deposition, a shutter was used and the boat was then

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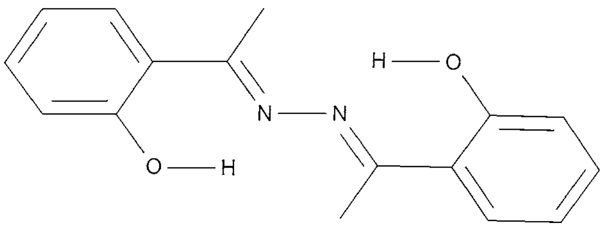

Figure 1 The molecular structure of *o*-hydroxy acetophenone azine.

gradually heated until the material started to evaporate at the desired deposition rate (~5 nm/s). On removing the shutter, molecules leaving the source as vapor were deposited on the substrate surface held at room temperature (~300 K). The deposition rate was kept nearly constant during the evaporation process at ~5 nm/s. Several trials were conducted to adjust the conditions of evaporation, in order to avoid decomposition of the material by overheating during evaporation and to obtain films with nearly stoichiometric composition. The film thickness, d, was determined by a quartz crystal thickness monitor (Edwards, FTM4) and also interferometrically measured applying Tolansky's method [8].

2.3. Structural characterization techniques

The X-ray diffraction (XRD) analyses of the powder, and the deposited films of ortho-hydroxy acetophenone azine ($C_{16}H_{16}N_2O_2$) were carried out using an X-ray diffractometer (Type Shimadzu, Model XD-D1) with Ni-filtered Cu K_α radiation. FTIR spectra of the bulk (as KBr disc) and deposited thin films (onto a KBr single crystal substrate) of the compound under investigation were carried out using an ATI Mattson, Infinity series FTIR. The transmittance, T, and reflectance, R, of the deposited films of ortho-hydroxy acetophenone azine onto quartz substrates, at normal incidence of light in the wavelength range from 200 nm to 2100 nm were measured by a double beam spectrophotometer (Type JASCO Corp., Model V-570).

3. Results and discussion

3.1. Structural characterization

X-ray diffraction patterns of the powder of ortho-hydroxy acetophenone azine and its film of the same thickness (500 nm) deposited onto a glass substrate with a deposition rate ~5 nm/s, are shown in Fig. 2a and b respectively. The pattern (Fig. 2a) corresponds to a single-phase ortho-hydroxy acetophenone azine of the monoclinic system with preferred orientation, where the (020) reflecting plane is the predominant plane. The lattice parameters were determined by introducing the X-ray data produced by the X-ray diffractometer into a Treor X-ray program and were found to be $a = 1.578$ nm, $b = 1.394$ nm, and $c = 0.647$ nm. The plane angles were found to be $\alpha = 90°$, $\beta = 123.8°$, and $\gamma = 90°$ (see Table I).

3.2. FTIR assignment of *o*-HAcPhAz

The FTIR spectra in the range 4000–500 cm^{-1} of *o*-HAcPhAz of the bulk and thin films are shown in Fig. 3a and b. As shown from the figure they were similar to each other.

Salicylaldazine was previously found to have a C_{2h} symmetry from an X-ray study [9] and from using IR

TABLE I X-ray analysis of *o*-HAcPhAz powder and thin film ($d = 500$ nm)

Powder form	From the program		Thin film form
2θ (Experimental)	2θ (calcul.)	(*hkl*)	2θ (Exp.)
6.745	9.732	(100)	–
12.684	12.691	(020)	12.685
13.893	13.888	(−101)	–
14.905	14.914	(210)	–
17.625	17.927	(−301)	–
–	17.668	(011)	–
22.555	22.556	(−401)	–
25.275	25.315	(031)	–
26.465	26.442	(140)	–
–	27.923	(410)	–
–	27.986	(−202)	–
27.995	27.996	(330)	–
29.185	29.186	(−141)	–
–	31.703	(−422)	–
321.735	31.723	(−502)	–
33.945	33.938	(012)	–
–	38.667	(032)	–
–	38.681	(151)	–
38.705	38.728	(060)	–

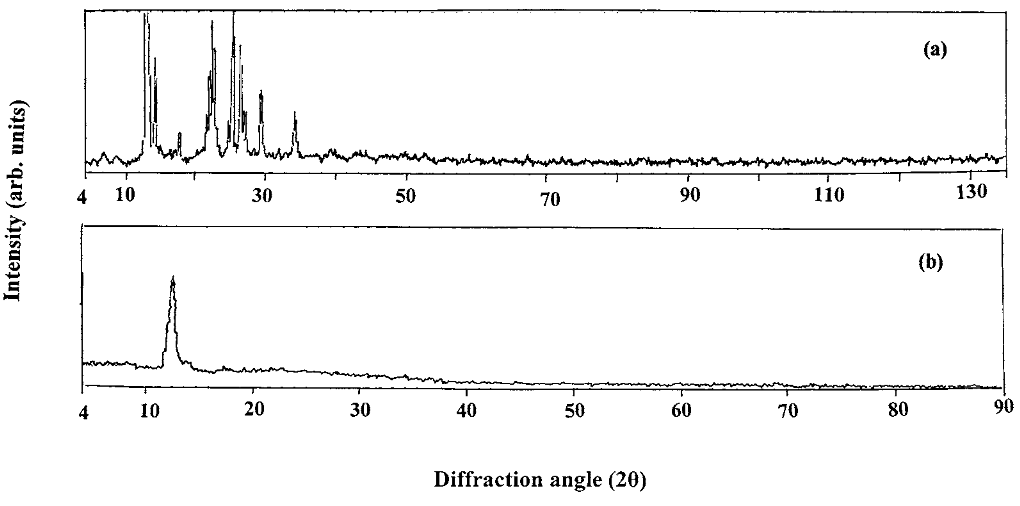

Figure 2 X-ray diffraction patterns of *o*-hydroxy acetophenone azine. (a) Bulk material. (b) As-deposited film.

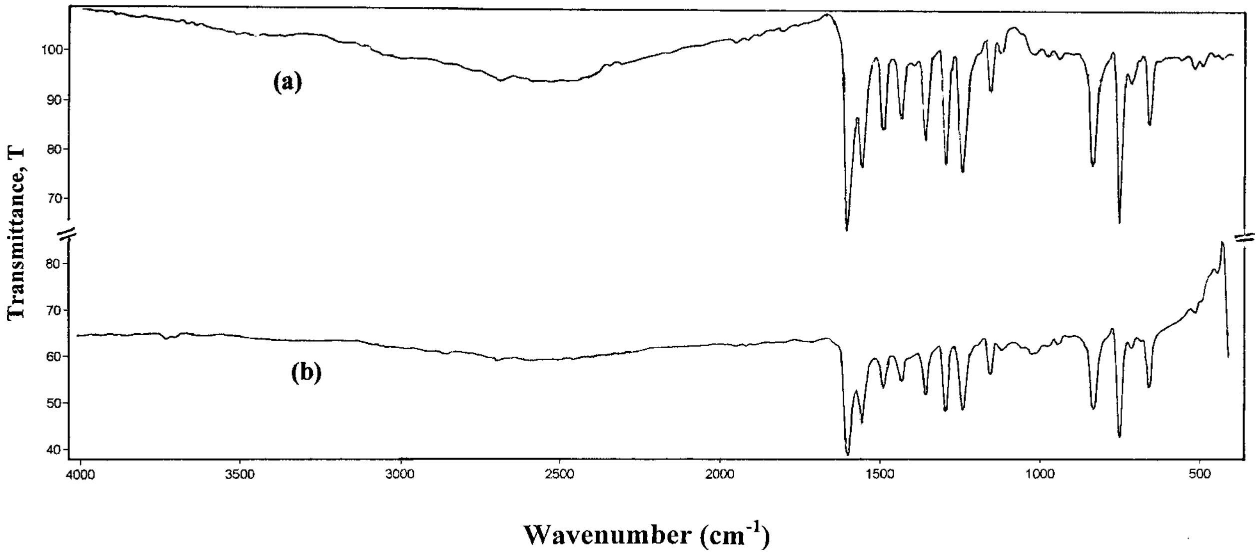

Figure 3 The FTIR spectra of (a) powder (as KBr disc) and (b) as-deposited film (onto KBr single crystal substrate) of *o*-hydroxy acetophenone azine.

and Raman spectroscopy in the solid phase and in solution [10, 11]. The *o*-HAcPhAz compound is analogous to salicylaldazine and it is reasonable to expect it to belong to the C_{2h} point group. Its vibrations can thus be distributed as $\Gamma\text{vib.} = 35A_g + 34B_u + 17A_u + 16B_g$. The small number of the IR bands reflect the symmetric nature of this molecule. The OH stretch appears as a medium broad band at 3430 and 2750 cm^{-1}. The νN–N stretch expected in the range 1100–1000 cm^{-1} [11, 12] is not observed for *o*-HAcPhAz likewise, the ν_a C=N stretch is observed at 1605 cm^{-1} with a very strong intensity, while the symmetric component ν_s C=N expected at about 1550 cm^{-1} is not found [10]. Hence, it is reasonable to conclude from the IR spectra that *o*-HAcPhAz exhibits approximately a C_{2h} molecular symmetry [10, 12]. It should be noted that ν_a C=N for *o*-HAcPhAz is observed at a lower frequency compared to Salicylaldazine (ν_a C=N: 1623 cm^{-1}) [10]. This may be attributed to a hyperconjugation effect of the two methyl groups. However, the absence of coupling between the deformation δCH and ν_a C=N may also reduce the ν_a C=N frequency. Two strong bands are observed in the range 1300–1200 cm^{-1}. The two bands at 1300 and 1247 cm^{-1} represent the two bands (ν-O-Ph) and (ν-C-Ph) respectively. These two modes were found for Salicylaldazine at 1280 and 1207 cm^{-1} respectively [10, 11]. The symmetric component ν_s C–(CH_3) Ph is observed at 839 cm^{-1} [10]. The assignment of the remaining absorptions are made following Salicylaldazine assignment [10, 11].

3.3. Optical constants

The evaluation of the optical constants (n and k) from both, the measured values of T and R, (after correcting for the transmittance and reflectance of the substrate, and the incoherent multiple reflections inside the transparent substrate) and the determined value of film thickness, d, were carried out using a simple computer program. The absorption coefficient (α) could be calculated from the experimental values of T, R and d by using the following relation [13].

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{4T^2} + R^2\right]^{0.5}\right] \quad (1)$$

The extinction coefficient, k, is related to the absorption coefficient, α, by the relation

$$k = \alpha\lambda/4\pi \quad (2)$$

where λ is the wavelength of the incident beam.

From the reflectivity, R, of the material and the extinction coefficient, k, the refractive index, n, could be computed using the relation [14]

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (3)$$

and consequently all the other optical parameters could be determined.

The tansmittance, T, and reflectance, R, for five films in the thickness range of 100–200 nm were used for computing the optical constants (n and k).

For example, the typical spectral behaviours of both transmittance, T, reflectance, R, and $T + R$ at normal incidence of light in the wavelength range 200–2100 nm for *o*-HAcPhAz film with thickness 120 nm, is shown in Fig. 4. The spectral dependence of both refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ are shown in Fig. 5, taking into account that the values used in the plots are the mean values of both $n(\lambda)$ and $k(\lambda)$ determined from the five films of different thicknesses (100, 120, 150, 170 and 200 nm). From Fig. 5, one can conclude the following features:

i. The analysis of the accuracy of the adopted technique gave ± 1.0 and $\pm 0.5\%$ for the n and k respectively.

ii. Both n and k were practically independent on film thickness in the range 200–2100 nm.

iii. The refractive indices, n, of the *o*-HAcPhAz thin films show as a function of wavelength anomalous dispersion in the spectral range 520–1000 nm.

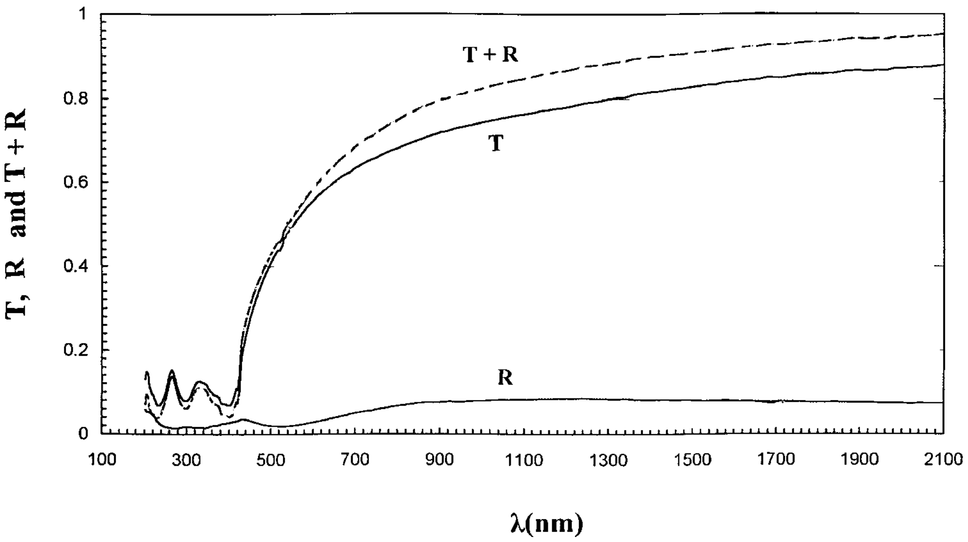

Figure 4 $T(\lambda)$, $R(\lambda)$ and $T + R$ (λ) for as-deposited *o*-hydroxy acetophenone azine films (as representative example $d = 120$ nm).

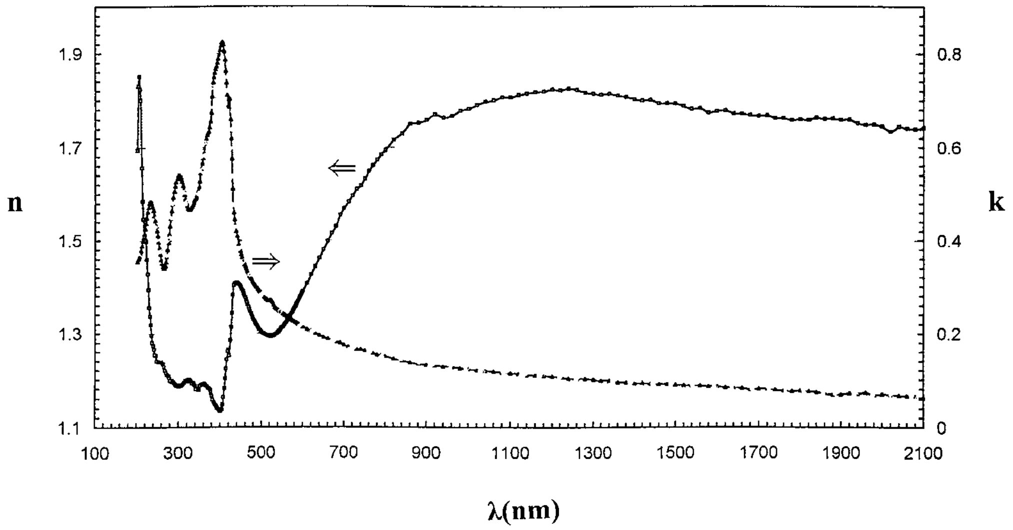

Figure 5 $n(\lambda)$ and $k(\lambda)$ for *o*-hydroxy acetophenone azine as-deposited films.

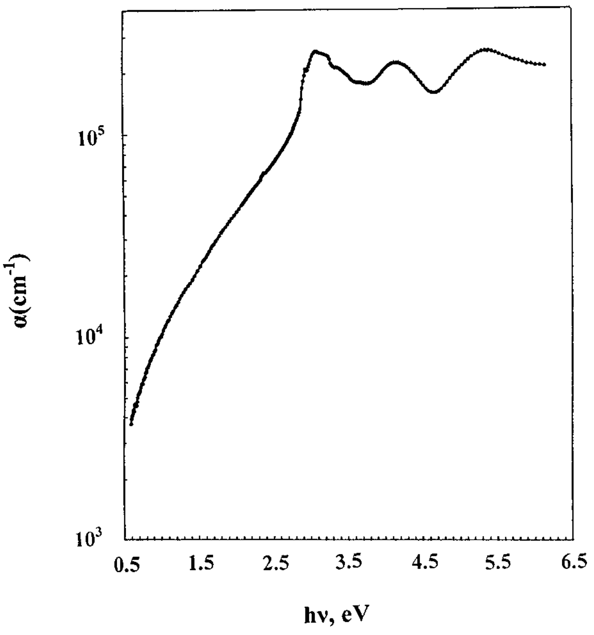

Figure 6 The absorption coefficient (α) as a function of $h\nu$ for as-deposited *o*-hydroxy acetophenone azine films.

The absorption coefficient (α) of *o*-HAcPhAz films as a function of $h\nu$ is shown in Fig. 6, where the absorption coefficient values were derived using Equation 2. From the figure, the following energy gaps corresponding to the observed maximal optical transitions have been calculated ($E_g = 2.82$, 3.13, 4.21 and 5.52 eV). The figure shows three intense bands and a shoulder, which were designated as the following: the A-band appears at 232 nm, and B-band has its maximum absorption at 299.5 nm, while C-band was observed at 440.6 nm with a shoulder at 404.8 nm. The observed three bands A, B and C are attributed to $\pi^* \leftarrow \pi$ transitions although $\pi^* \leftarrow \sigma(n)$ transitions are allowed and constitute part of the C-band. The appearance of the C-band in the spectrum (Fig. 6) of *o*-HAcPhAz can be ascribed to the presence of hydroxyl groups in the orthopositions to the aldimino groups (–CH=N–) which can coordinate with nitrogen via hydrogen bonding O–H $\cdots$ N, which increases the delocalisation of the π-electrons.

The plot of n^2 versus λ^2 as shown in Fig. 7 gives a straight line in the longer wavelength region of the

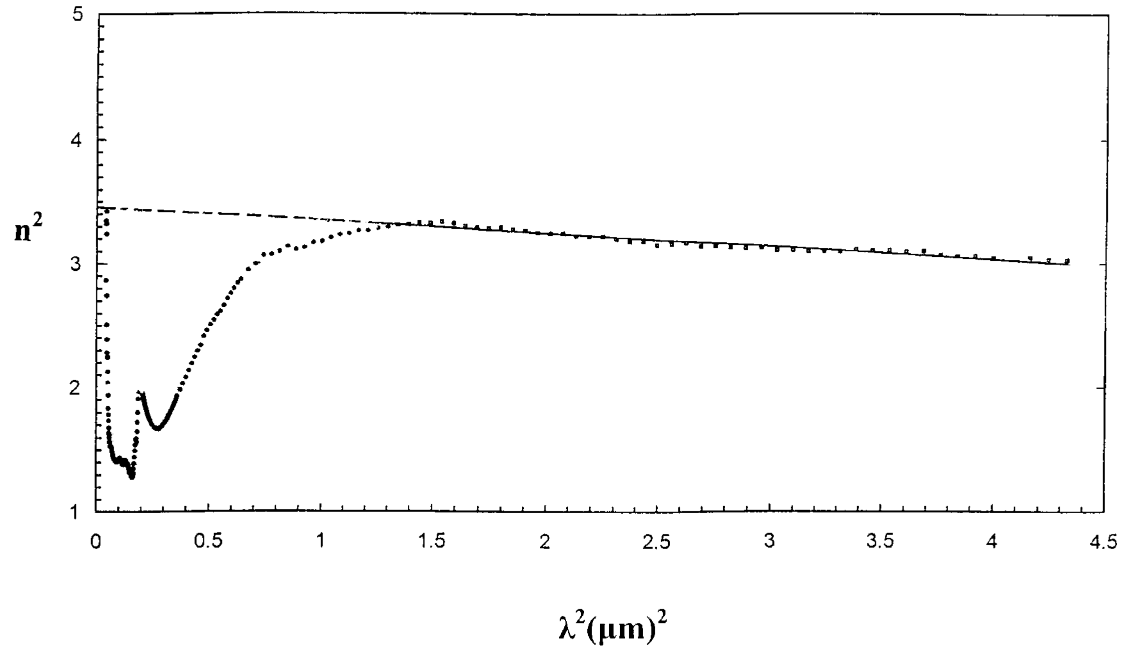

Figure 7 n^2 versus λ^2 for as-deposited *o*-hydroxy acetophenone azine films.

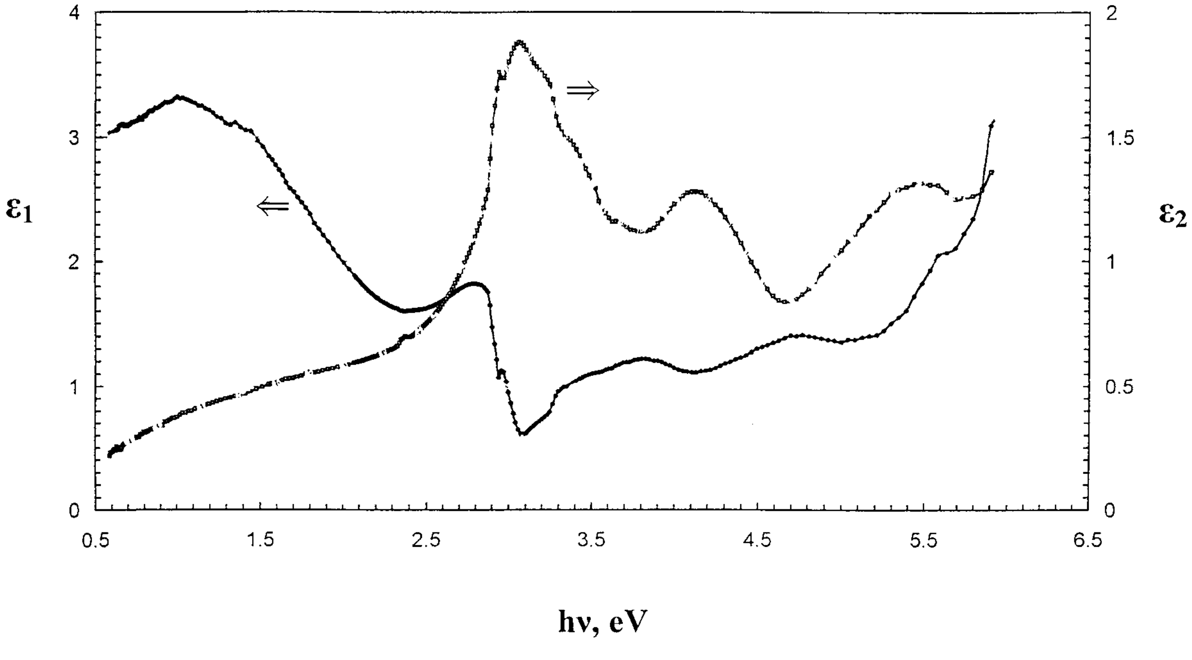

Figure 8 The variation in real and imaginary parts of the dielectric constants (ε_1, ε_2) as a function of photon energy $h\nu$ for as-deposited *o*-hydroxy acetophenone azine films.

spectrum. The extrapolated figure with the ordinate (n^2) at zero wavelength gives the high frequency dielectric constant (ε_∞) to be 3.457 at room temperature for the compound films. This value is similar to the organic semiconductor materials such as $\varepsilon_\infty = 2.56$ (at 300 K) for bistetramethyl traselenafulvalene-x [$(TMTSF)_2\ A_5F_6$] [15].

The real and imaginary parts of the dielectric constants ($\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$) of *o*-HAcPhAz films were calculated and plotted against $h\nu$ in Fig. 8. This figure shows that ε_1 decreases fast from 1.0–3.07 eV, attains a maximum at 3.07 eV and then slowly falls down with another two peaks at energies 4.17 and 5.51 eV.

The spectral behaviour of the real, $\sigma_1 = \varepsilon_2\omega/4\pi$, and imaginary $\sigma_2 = [(1-\varepsilon_1)\omega/4\pi]$, parts of the optical conductivity against $h\nu$ are shown in Fig. 9. The plot of $\sigma_1 = f(h\nu)$ shows four maxima at 2.82, 3.07, 4.17 and 5.51 eV, which are in agreement with those observed in $\varepsilon_2 = f(h\nu)$ plot. The graphical representation of $\varepsilon_2 = f(h\nu)$ (Fig. 9) shows also four optical transitions at 2.82, 3.07, 4.17 and 5.51 eV, which are similar to those of Fig. 8.

The obtained results can be analyzed through graphical representations of volume energy loss $-\mathrm{Im}(1/\varepsilon) = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2)$, surface energy loss, $-\mathrm{Im}(1/\varepsilon + 1) = \varepsilon_2/[(\varepsilon_1 + 1)^2 + \varepsilon_2^2]$ and surface energy loss/volume energy loss against $h\nu$ are shown in Fig. 10. It has been

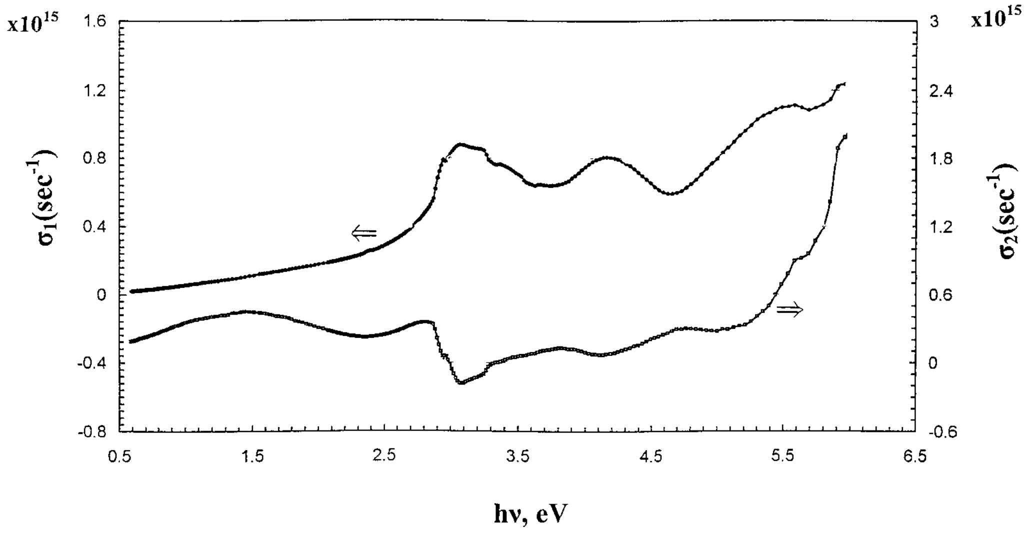

Figure 9 The variation in real and imaginary parts of the optical conductivity (σ_1, σ_2) as a function of $h\nu$ for as-deposited *o*-hydroxy acetophenone azine films.

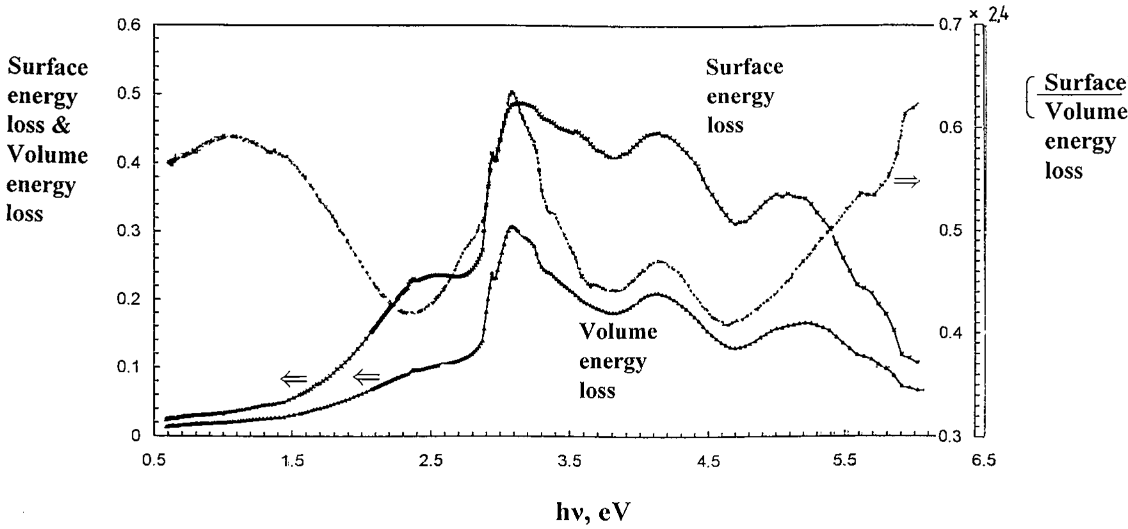

Figure 10 Surface, volume and surface/volume energy loss as a function of $h\nu$ of *o*-hydroxy acetophenone azine films.

shown from the figure that the same optical transitions appeared.

4. Conclusions

The obtained X-ray results revealed one peak with a preferred orientation (020) plane in the thin film of the compound under investigation with the disappearance of the other peaks observed in its powder form, which means that it can be obtained nearly as a single crystal. The FTIR assignment showed that the structure of the compound is preferred as a C_{2h} point group in its solid phase in both of powder and thin film. The optical analyses of the *o*-HAcPhAz have indicated the presence of four optical transitions. The obtained optical values of dielectric constants and conductivity show that this compound can be used in dielectric and photo-semiconductors technologies.

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