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Characterization of oligothiophene films by high resolution electron energy loss spectroscopy

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Abstract

Electronic structures of quinquethiophene (5T) and sexithiophene (6T) polycrystalline films deposited by evaporation on gold substrates were studied by high resolution electron energy loss spectroscopy (HREELS). Vibrational spectra were compared to infrared spectroscopy and Raman scattering results. They reveal that surfaces are not rough and are free from contaminants. Energy gap values of 2.38 ± 0.02 and 2.27 ± 0.02 eV for 5T and 6T films, respectively, were evaluated from electronic spectra. Comparison with optical spectroscopy enabled the assignment of losses corresponding to optically allowed and forbidden transitions. Some of the latter ones located at 1.2, 1.7 and 2.0 eV were observed in 5T films and were assigned to $S_0 \rightarrow T_n$ transitions. Differential cross section analysis reveals the presence of resonance processes in the excitation mechanism. Ionization potentials were estimated to be 4.7 ± 0.5 eV for both films.

Keywords: Conducting polymers; High resolution electron energy loss spectroscopy; Thiophenes; Triplet states; Resonances

1. Introduction

Thiophene oligomers (*n*T, where *n* stands for the number of thiophene rings) are widely investigated materials for light emitting devices (LED) and field-effect transistors (FET). In order to improve the properties of new organic electronic devices, a detailed understanding of the excitation and relaxation mechanisms is needed. Although a lot of theoretical and experimental studies on isolated molecules have been performed [1], little knowledge exists on their solid state electronic structure [2].

High resolution electron energy loss spectroscopy (HREELS) is a powerful tool for the investigation of thin films [3]. In a HREELS experiment, an incident low energy electron beam interacts with the surface region exciting vibrational modes [3], electronic states [4] and secondary emission [5]. Intensity of the backscattered electrons is then measured either versus energy for a given direction, or versus analysis angle for a given energy loss. Depending on the mechanism (dipole, impact or resonance) [3], electron interactions can occur at different distances. In particular, impact interactions (of short range), which are produced at typical interaction distances of some Angstrom, are observed in off-specular conditions and enable optically forbidden transitions to be observed by HREELS. Among them, triplet excitation, only detected by indirect methods (e.g. delayed fluorescence [6]), is of particular interest. In fact, light emission is due to the relaxation of singlet states. Other non-radiative processes reduce the efficiency of such devices. One of these processes includes intersystem crossing from the singlet to the triplet manifold.

A few works employing low energy electrons as excitation probes for oligothiophenes (used as models of polythiophene) films, where transitions higher than the energy gap were detected, are reported in literature [7,8]. However, even using HREELS, the direct detection of the triplet state is not easy. In fact, the mechanism of electronic exci-

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tation frequently occurs via a resonance and, consequently, cross sections are peaked functions of the primary electron energy and of the geometrical conditions [9]. Moreover, since HREELS is a very sensitive surface technique, the elastic peak and vibrational region of the spectra were used to check roughness and possible contamination of the film surface, respectively. Complete spectra, containing losses from elastic scattering to total electron relaxation, were then recorded for increasing incident electron energies. They present features which can be assigned to optically allowed excitations. For a very limited set of experimental conditions, other loss features that appear at energy losses lower than the energy gap, not present in optical spectra, are assigned to the excitation of triplet states.

2. Experimental details

Oligothiophenes have been synthesized according to procedures described elsewhere [10]. Low roughness glass plates covered by thick layers of evaporated gold were used as substrates. Films about 100 nm thick of quinquethiophene (5T) and sexithiophene (6T) were evaporated on the gold substrates. To avoid surface contamination, samples were transferred under argon into the introduction chamber put under a nitrogen atmosphere by means of a glove bag. In the HREELS chamber, vacuum was of the order of 10^{-10} Torr.

Spectra were recorded using two different HREEL spectrometers: a Kesmodel LK 2000R and a Leybold Heraeus ELS 22 [5]. Reproducible vibrational spectra were obtained using both spectrometers, for samples prepared in identical conditions and studied with the same incident energy and geometrical arrangement. Electronic spectra have been entirely recorded using the Kesmodel system, which has adequate electron optics for losses ranging from 0 to 50 eV.

Incident electron energies, E_p, were used from 0 to 10 eV. Experimental resolution, taken as elastic peak FWHM, was better than 13 meV. Sweeping steps were about 0.33 meV for vibrational spectra and 5 meV for the electronic ones. Incident and backscattered electron directions are here referred to the normal of the sample surface.

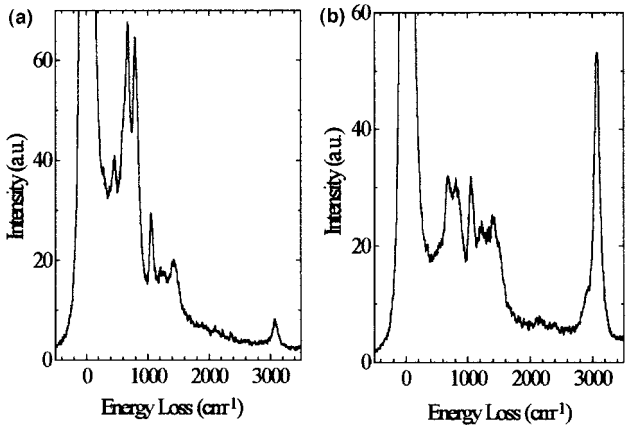

Fig. 1. Vibrational spectra of a 100 nm 6T polycrystalline film taken in specular conditions (incidence and analysis angles of 60°) for incident electron energy around 2 eV (a) and 7 eV (b).

Table 1

Assignment of main vibrational peaks in 6-thiophene HREEL, IR and Raman spectra

HREELS (cm^{-1})	Infrared (cm^{-1})	Raman (cm^{-1})	Assignment [12–14]
285			
		305	
459	450		Out-of plane ring deformation
590			
680	688		C–H out of plane + C–S stretch
		695	C–S–C ring deformation
		739	C–H out of plane + C–S stretch
797	791		C–S stretch
	832	833	C–H in plane or C–S–C stretch
1053	1046	1052	C–H in plane bending
1073	1070		C–C stretch
1221		1218	Intercycle stretch
1365		1367	C=C stretch
1424	1426		C=C stretch
	1441	1455	C=C stretch
1458		1461	C=C stretch
	1490	1510	C=C stretch
2920			C–H stretch (contaminant.)
	3045		C–H stretch
3066	3055	3071	C–H stretch
3085	3080	3100	C–H stretch

3. Results and discussion

3.1. Vibrational losses

Fig. 1 shows vibrational spectra of a 6T film recorded in specular geometry for incident energies of 2 and 7 eV. The high intensity of the elastic peak certifies a very low roughness of the film surface [11]. Intense losses in both spectra mainly correspond to infrared active modes similar to those of the bulk. Losses corresponding to Raman active modes (Table 1) were also detected. Through the low aliphatic C–H stretching contribution (cf. Fig. 1b), centered around 2920 cm^{-1}, one can conclude that film surface contamination is irrelevant.

3.2. Electronic losses

In Fig. 2a, a set of electronic spectra of a 5-thiophene film recorded for different primary electron energies ranging from 3 to 7 eV is presented.

Energy losses range from zero (elastic peak) to the total relaxation. One can clearly distinguish the vibrational loss

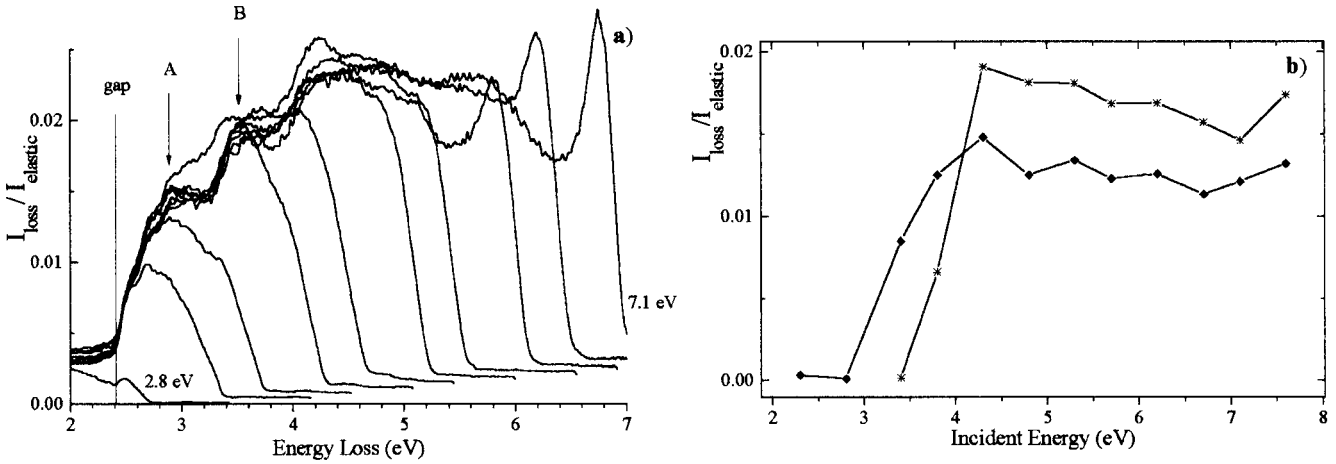

Fig. 2. (a) Electronic spectra of a 5-thiophene film for primary electron energies ranging from 2.8 to 7.1 eV with a step between 0.4 and 0.5 eV. Incident angle was 60° and analysis angle was 30°. Spectra are normalized to the elastic peak. (b) Analysis of I_{loss}/I_{elast} of losses A and B at 2.9 (♦) and 3.5 eV (★), respectively, versus incident energy.

region near the elastic peak superimposed onto an exponential background due to the electron scattering at the film surface. In all spectra, a continuum structured band appears with a threshold of 2.38 ± 0.02 eV (the uncertainty is related to the elastic peak FWHM). This continuum band corresponds to interband transitions and the threshold of the band gap of the system [8,15]. Differential cross sections of losses centred around 2.9 eV (A) and at 3.5 eV (B) were evaluated by the ratio between the loss intensity and that of the elastic peak (Fig. 2b). Resulting curves as a function of the incident energy display a behaviour typical of a mixed mechanism of electron excitation: dipolar and impact testifying the optically allowed character of these losses. Loss B agrees with the maximum absorption in the film optical spectrum obtained with polarized light parallel to the long molecular axis.

Fig. 3a shows a set of complete spectra of 6T film for primary energies ranging from 3.2 to 8.7 eV. For these films, an energy gap value of 2.27 ± 0.02 eV was found. Differential cross sections of losses centred around 2.7 eV (C) and 3.5 eV (D) were evaluated as described (see Fig. 3b). They present one maximum located around 6.8 eV.

The behaviour of these differential cross sections versus primary energy is typical of a resonance process involving the formation of a negative ion. In this kind of process, the incident electron is trapped in one of the molecule antibonding orbitals, forming a temporary negative ion. Its subsequent relaxation, followed by the ejection of an electron, can leave the system in an excited state (vibrational or electronic) or in a dissociative state. Electron exchange processes accompanying this mechanism are responsible for the production of triplet states. The occurrence of resonances can also explain possible film degradation which also produces that of the electronic device.

Recently, triplet states have been detected for different thiophenes by delayed fluorescence measurements [6]; for 6T films, a triplet state, supposed to be the lowest one, was found around 1.8 eV. HREEL spectra of 5T films (Fig. 4a)

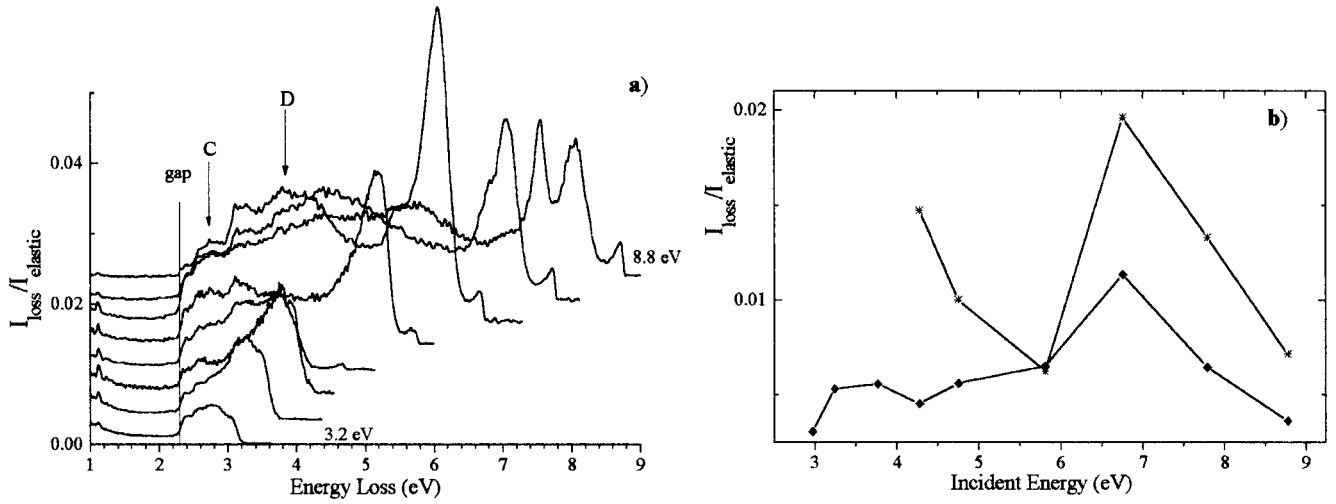

Fig. 3. (a) Electronic spectra of a 6T film for primary electron energies of 3.2, 3.7, 4.2, 4.7, 5.7, 6.7, 7.8 and 8.7 eV. Incident angle was 60° and analysis angle was 30°. Spectra are normalized to the elastic peak. (b) Analysis of I_{loss}/I_{elast} of losses C and D at 2.7 (♦) and 3.5 eV (★), respectively versus incident energy.

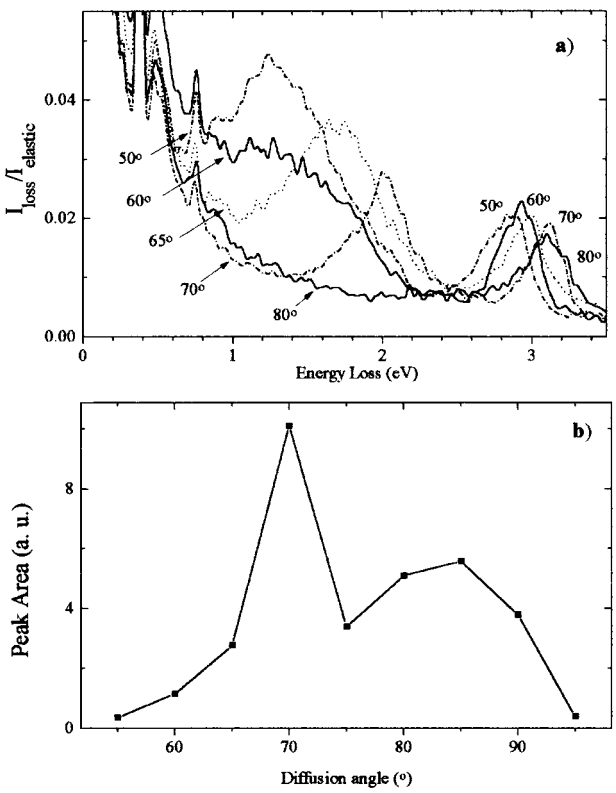

Fig. 4. (a) HREEL spectra of 5T films, recorded for a primary energy of 3.2 eV and an incident angle of 45° at different analysis angles. (b) Area of the fitted peak to the 1.7 eV loss as a function of the diffusion angle, for the same primary energy and incident angle is shown.

were recorded for a primary energy of 3 eV and for incident angle of 45° and different angles of analysis. Three intense features centred at 1.2, 1.7 and 2.0 eV displayed in Fig. 4a are here assigned to triplet excitations existing in the band gap. The two first values agree with the ones found in the literature for the films measured by delayed fluorescence [6] and for the isolated molecules by photo-acoustic calorimetric measurements [16] and theoretical calculations [17]. The area of the fitted peak to the 1.7 eV loss profile as a function of the diffusion angle is shown in Fig. 4b. The resonance nature of the loss is revealed by the existence of a maximum in the variation of I_{in}/I_{elast} versus the diffusion angle.

Ionization potential can be evaluated from HREEL spectra taking into account secondary emission. In fact, the threshold can be measured from the lowest primary energy producing a spectrum that exhibits secondary emission. For 5T and 6T films, this threshold can be estimated to be 4.7 ± 0.5 eV. The measurement accuracy stands for the primary energy interval between two consecutive spectra. This is in good agreement with values taken from ultraviolet photoelectron spectroscopy (M. Bungs, pers. commun.), which gives an ionization potential around of 5 eV.

4. Conclusions

Electronic excitations of 5T and 6T oligomeric films of thiophene were studied. Vibrational spectra assured that films were flat and contamination free. Electronic spectra led to energy gap values of 2.38 ± 0.02 and 2.27 ± 0.02 eV for 5T and 6T films, respectively. In 5T films, losses located at 1.2, 1.7 and 2.0 eV were here assigned to $S_0 \rightarrow T_n$ transitions. The observation of strong secondary emission threshold led to the evaluation of ionization potentials of 4.7 ± 0.5 eV for both films.

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