

PHOTOELECTRON AND PENNING IONIZATION ELECTRON SPECTROSCOPIC INVESTIGATION OF TRIMETHYLSILYL- AND t-BUTYL-THIOPHENES

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Summary

Penning ionization electron spectroscopy and CNDO/S calculations have been successfully applied to the analyses of the UV photoelectron spectra of 2- and 2,5-bistrimethylsilylthiophene and 2-t-butylthiophene. The relative intensities of the π type bands are greatly enhanced in the Penning spectra compared with those of the UV photoelectron spectra.

Penning Ionization Electron Spectroscopy (PIES) has been successfully applied to the analyses of the UV photoelectron spectra (UPS) of some unsaturated molecules [1–3]. The most remarkable difference between the photoelectron and Penning electron spectra is that the π bands in the Penning spectra are enhanced relative to the σ bands. This feature was used along with quantummechanical calculations, in our previous paper [4] for the investigation of the photoelectron spectrum of trimethylphenylsilane and led to successful analyses of the UPS.

In this work a detailed assignment of the bands in the UPS of 2-trimethylsilyl- (I), 2,5-trimethylsilyl- (II) and 2-t-butylthiophene (III) has been made on the basis of modified CNDO/S calculations [5] and the Penning spectra.

Experimental

The electron spectra were obtained at an ejection angle of 90° with respect to the metastable or the photon beams by means of a hemispherical analyzer. The sample vapor was introduced into the collision chamber through a sample nozzle at ca. 25°C . Metastable neon atoms, Ne^* (3P_2 16.62 eV) were produced by impact of 60 eV electrons; at this energy the contributions of Ne^* (3P_0 16.72 eV) atoms and

photons were negligible [4]. For the measurement of the UPS pure helium and neon gases were discharged to produce the He(I) (21.21 eV) and Ne(I) (16.85 and 16.67 eV) radiations; the low energy component of the resonance lines of the latter made little contribution to the spectra.

Results and discussion

In Figs. 1 and 2 the Ne(I) photoelectron and Ne* Penning spectra of the investigated compounds are presented; it should be noted that the *IP* scales in the figures refer only to the UPS. In the case of PIES the abscissas correspond to the energy of ejected electrons (approximately $IP = 16.62 \text{ eV} - E_{e1}$, where E_{e1} is the kinetic energy of the emitted electron). On Figs. 1 and 2 the assignment of the π bands is unambiguous. We find that the first two bands due to the π_2 and π_3 orbitals

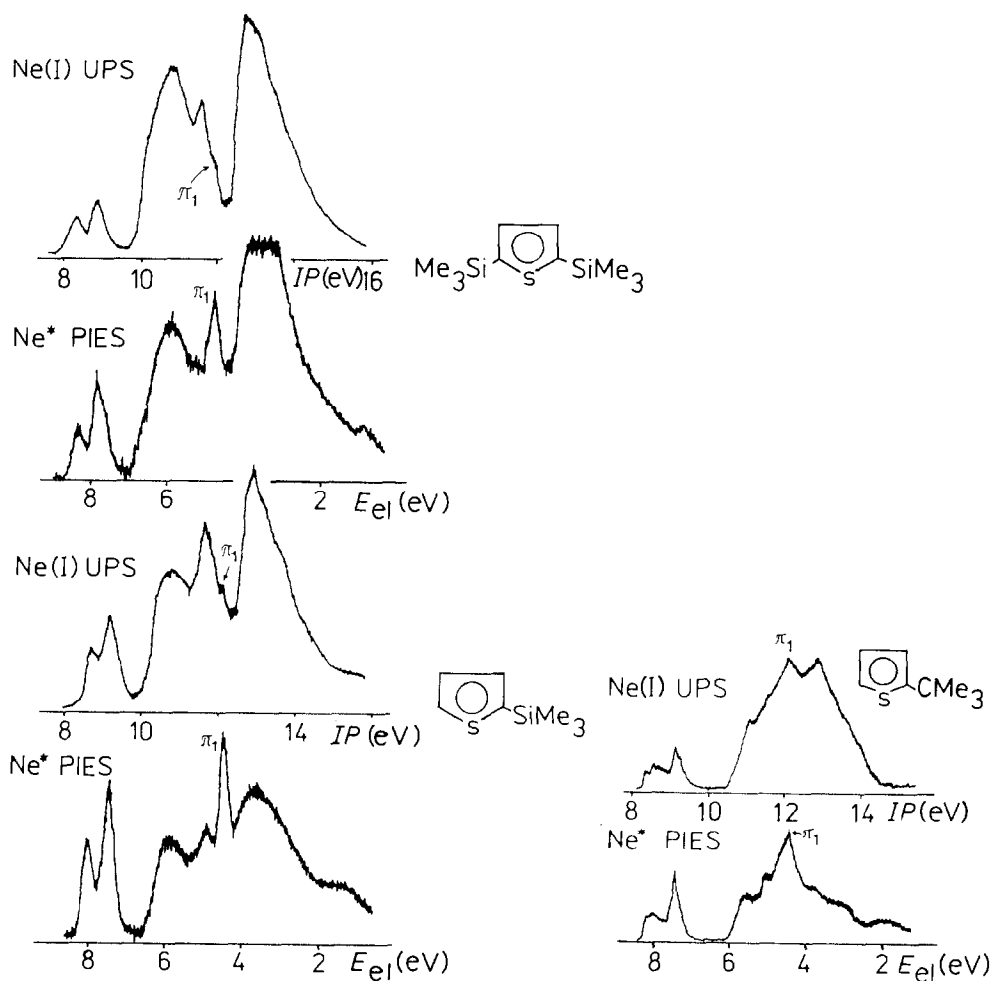


Fig. 1. UP and PIE spectra of trimethylsilylthiophene.

Fig. 2. UP and PIE spectra of 2-t-butylthiophene.

of thiophene are enhanced in the PIES, in agreement with the trend mentioned before. Similarly, we can assign the bands around 12 eV in the UPS to the π_1 orbitals. In PIES they give sharp strong peaks, while in the UPS there is a weak band (Fig. 1) or a shoulder (Fig. 2) in the corresponding region.

Figure 3 shows the spectrum of compound I together with those of the two reference compounds [6]. In this case the He(I) spectra were used for better comparison. Comparing the three spectra, we find that the first two peaks of I are derived from the π_3 and π_2 orbitals of the thiophene moiety. Further, it is obvious that the wide band at 10–11 eV is due to the Si–C bond. The next sharp band at 11.68 eV originates from thiophene and has σ character according to the results of PIES [2]. It is interesting that the π_1 band at 12.12 eV, which gives a sharp peak in the He(I) spectrum, shows a diffuse band in the Ne(I) spectrum. Similar features have been found in the other investigated molecules. The bands in the region higher than 12.5 eV can be assigned to the orbitals of the methyl groups.

The spectrum of compound II has a similar structure and the assignment is also similar to that for compound I. Naturally, the relative intensity of the bands connected with the trimethylsilyl groups are increased in the compound II. Taking account of the position of the π_1 band, we can also assign the bands in the spectrum of (III).

In Table 1 are shown the observed ionization potentials together with those calculated by the CNDO/S method. In our previous investigation [5] a linear correlation formula

$$IP_i = -0.74\varepsilon_i + 1.70 \text{ eV}$$

(where ε_i is the orbital energy) was found to give good results. The calculated values in Table 1 have been corrected by use of this formula.

The calculations were carried out with (CNDO/S d) and without d orbitals

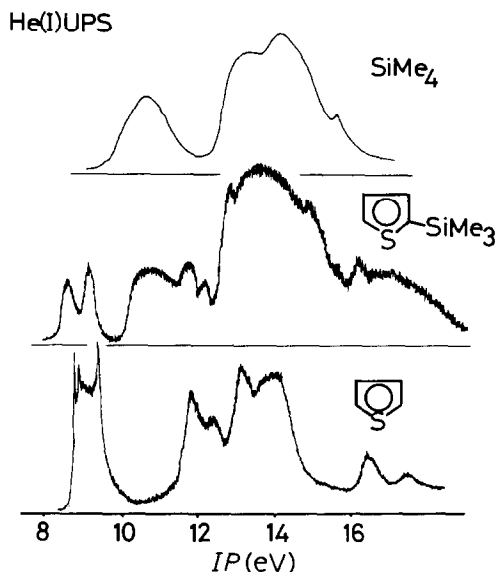


Fig. 3. The UP spectra of 2-trimethylsilylthiophene and the reference compound SiMe₄ and thiophene.

TABLE I
OBSERVED AND CALCULATED IONIZATION POTENTIALS (eV)

2-Trimethylsilylthiophene ^a			2,5-Bis(trimethylsilyl)thiophene			2-t-Butylthiophene ^a		
Exp.	CNDO/S	CNDO/S _d	Exp.	CNDO/S	CNDO/S _d	Exp.	CNDO/S	CNDO/S _d
8.68	8.34 π_3	8.63 π_3	8.40	8.15 a_2 (π_3)	8.52 a_2 (π_3)	8.32	8.15 π_3	
9.22	9.36 π_2	9.31 π_2	8.90	9.29 b_1 (π_2)	9.26 b_1 (π_2)	9.10	9.40 π_2	
10.4-11.3	{ 10.19 Si-C _{Ar}	10.25 Si-C _{Ar}	10.20	{ 9.73 b_2 Si-C _{Ar}	9.78 b_2 Si-C _{Ar}	10.98	10.84 a_1 (n)	
	{ 10.83 SiC ₃	10.91 SiC ₃		{ 10.40 a_1	10.54 a_1		{ 11.61 C-C ₃	
11.68	{ 11.08 SiC ₃	11.13 a_1 (n)	10.5-11.1	{ 10.80 a_1 (n)	10.87 a_1 (n)	11.55	{ 11.62 C-C ₃	
	{ 11.14 a_1 (n)	11.13 SiC ₃		{ 10.82 a_1 SiC ₃	10.93 b_2 SiC ₃		11.68 π_1	
12.12	12.14 π_1	12.22 π_1	11.56	{ 10.83 b_2 SiC ₃	10.94 a_1 SiC ₃	12.05	{ 12.34 CH ₃	
12.75	{ 12.67 b_2	12.73 b_2		{ 11.28 b_2 SiC ₃	11.31 b_1 SiC ₃		{ 12.70 CH ₃	
	13.0-14.4	{ 13.12 b_2	13.27 b_2	11.92	{ 11.38 a_1 (n)	11.47 a_1 (n)	12.8	{ 12.97 CH ₃
{ 14.33 a_1		14.42 a_1	12.75	{ 12.15 b_1 (π_1)	12.24 b_1 (π_1)	{ 13.01 b_2		
13.0-14.4	{ 14.58 CH ₃	14.50 CH ₃	12.75-15	{ 13.95 a_1	14.08 a_1			
	{ 14.85 CH ₃	14.84 CH ₃		{ 14.44 b_2	14.49 b_2			
	{ 15.31 CH ₃	15.37 CH ₃		{ 14.54 a_2	14.49 a_2			
	{ 16.05 CH ₃	16.07 CH ₃		{ 14.54 b_1	14.57 b_1			
	{ 16.31 CH ₃	16.47 CH ₃		{ 14.58 a_1	14.57 a_1			
				{ 14.98 b_2	15.00 b_2			
				{ 15.23 a_2	15.32 a_2			

^a Group theoretical assignments refer to the thiophene.

(CNDO/S). Table 1 shows that there are no substantial difference between the results obtained by the two methods except for the well-known stabilization effect of *d* orbitals. The spectrum in the region between 10 and 11.3 eV is related to three orbitals for the compound I and six for the compound II, and the lowest orbital corresponds to the Si-C_{Ar} bond in both cases. Probably the shoulder at 10.2 eV in the spectrum of II can be attributed to the Si-C_{Ar} bond.

In the spectrum of compound III there are three bands between the π_1 and π_2 bonds. The first of them at 10.98 eV can be related to the a_1 (σ) orbitals of thiophene and the second and third to the C-C bonds of the t-butyl group. Since these two are very close to one another, they are not resolved in the spectra.

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