Photoelectron Angular Distribution Measurements for Some Pyridines

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The angular distributions for the He I photoelectron spectra of pyridine, pentafluoropyridine, and 2,6-lutidine have been measured in order to solve the ambiguities on the band assignment of pyridine. It has been concluded that the first band of pyridine is assigned to the a_1n orbital and the fifth band to the lowest occupied $b_1\pi$ orbital.

The photoelectron differential cross-section $(d\sigma/d\Omega)$ for an unpolarized light and an ensemble of randomly oriented molecules or atoms is given by

$$d\sigma/d\Omega \propto 1 + 0.5\beta(1.5\sin^2\theta - 1), \quad (1)$$

where β is an asymmetry parameter and θ is the angle between the direction of an ejected photoelectron and that of an incoming photon.[1,2] The asymmetry parameter β depends on the kinetic energy of the photoelectron and the character of the molecular orbital from which the photoelectron is ejected. Therefore, the determination of the β value is useful for interpretation of photoelectron spectra. Especially, it is useful for the assignments of the overlapping bands which are difficult to be assigned solely by analysis of the ionization energies.

We reported in a previous paper[3] that the second and third bands of benzene, the assignments of which were in dispute, were assigned to the $e_{2g}\sigma$ and $a_{2u}\pi$ orbitals, respectively, by the comparison of the β values of benzene with those of hexafluorobenzene. In this paper the He I photoelectron angular distributions for pyridine, pentafluoropyridine, and 2,6-lutidine are reported and the assignments of the photoelectron spectral bands of pyridine are discussed.

Historically, concerning the assignments of the first three photoelectron spectral bands of pyridine there have been some conflicting proposals[4–12] (see also references 13—16). At present, however, there is no doubt that the broad band around 9.7 eV contains the a_1n and $a_2\pi$ bands and that the third band around 10.6 eV is related with the $b_1\pi$ orbital.[7,9–12,16] As for the band order of the first and second bands Heilbronner and co-workers assigned the first band to the a_1n orbital and the second band to the $a_2\pi$ orbital on the basis of band shape consideration and also of the methyl and trimethylsilyl-substituent effect.[7,9–11] On the other hand, King and co-workers prefer the reverse order on the basis of the fluoro-substituent effect.[12] In order to solve this problem we compare the photoelectron angular distributions for pyridine with those for 2,6-lutidine the band assignments of which are definite.[11] In addition to this, we examine the photoelectron angular distributions for the fourth and fifth bands of pyridine to certify their assignments by comparison with those of pentafluoropyridine.

Concerning the photoelectron angular distribution measurement for pyridine, Ames *et al.* presented crude data for the first three bands without giving the asymmetry parameter values.[17] Their data will be compared later with the present results.

Experimental

The details of the photoelectron spectrometer used for the photoelectron angular distribution measurements in this study were described in the previous paper.[3] The β values were obtained according to formula (1) using the intensities measured at the two angles, $\theta = 45°$ and $90°$. The measurements were carried out at room temperature and the vapour pressure of the samples was kept constant at 4×10^{-4} Torr.

Results and Discussion

The ionization potentials (IP) and the β values of pyridine, pentafluoropyridine, and 2,6-lutidine are summarized in Table 1. The error limits for β values in Table 1 denote mean square errors. The first, second, and third bands of the photoelectron spectra of pyridine and 2,6-lutidine are shown in Figs. 1(a) and (b), respectively, with the β values plotted against IP.

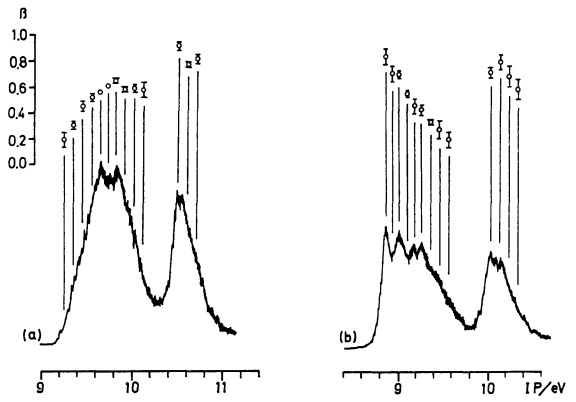

Fig. 1. The first, second, and third bands of the photoelectron spectra of pyridine (a) and 2,6-lutidine (b) and their β values.

We can see from Fig. 1 and Table 1 that the β values of the first and second bands of pyridine increase with increasing IP while the reverse is the case for 2,6-lutidine. This suggests that the order of the first and second bands of pyridine is reverse to that of 2,6-lutidine. The first band of 2,6-lutidine is the $a_2\pi$ band and the second band is the a_1n band.[11] Therefore, the first band of pyridine is assigned to the a_1n orbital and the second band to the $a_2\pi$ orbital. The β values of the first and second bands of pyridine estimated from the values in the regions in which the band overlap is small are $\approx$0.2 and $\approx$0.6, respectively (see Fig. 1(a) and Table 1), while those of 2,6-lutidine are $\approx$0.8 and

Table 1. The ionization potentials (IP in eV) and asymmetry parameters (β) of pyridine, pentafluoropyridine, and 2,6-lutidine

Pyridine		Pentafluoropyridine		2,6-Lutidine	
IP[a]	β	IP[a]	β	IP[a]	β
first and second bands		first band		first and second bands	
9.26	0.19±0.06	10.07	0.63±0.03	8.87	0.83±0.06
9.36	0.30±0.03	10.25	0.61±0.03	8.94	0.70±0.06
9.46	0.45±0.04	10.44	0.57±0.05	9.02	0.69±0.03
9.56	0.52±0.03	10.63	0.57±0.04	9.12	0.54±0.03
9.66(I)	0.56±0.01			9.21	0.45±0.06
9.73	0.61±0.01	second band		9.28	0.42±0.04
9.80(II)	0.65±0.02	11.14	0.71±0.08	9.38	0.32±0.02
9.90	0.58±0.02	11.34	0.67±0.07	9.48	0.27±0.07
10.00	0.59±0.03	11.54	0.65±0.05	9.58	0.19±0.06
10.10	0.58±0.06				
		third band		third band	
third band		11.84	0.63±0.04	10.03	0.71±0.04
10.54	0.91±0.03	11.94	0.69±0.04	10.14	0.79±0.06
10.64	0.77±0.02	12.04	0.64±0.06	10.24	0.68±0.08
10.74	0.81±0.04	12.14	0.67±0.04	10.34	0.58±0.08
		12.24	0.65±0.03		
fourth band					
12.37	−0.16±0.03	fourth band			
12.48	−0.31±0.01	13.44	0.57±0.08		
12.65	−0.35±0.01	13.61	0.55±0.08		
12.75	−0.14±0.07	13.78	0.54±0.08		
		13.95	0.54±0.05		
fifth band					
13.07	0.12±0.04	fifth band			
13.17	0.26±0.03	14.22	0.33±0.05		
13.27	0.27±0.06	14.39	0.37±0.05		
13.37	0.27±0.02	14.56	0.33±0.04		
13.47	0.37±0.03	14.73	0.33±0.05		

a) The IP's underlined are the vertical ionization potentials.

≈0.2, respectively (see Fig. 1(b) and Table 1). The β value of the first band of pyridine corresponds to that of the second band of 2,6-lutidine and the β value of the second band of pyridine is nearly equal to that of the first band of 2,6-lutidine. This fact also supports the above assignments.

Ames *et al.* presented crude photoelectron angular distribution data for pyridine and diazabenzenes without giving β values.[17] Their data indicate a general tendency that the band assignments for the first two bands of pyridine are consistent with the present conclusion.

IP (I) and IP (II) in Table 1 have so far been adopted as the vertical ionization potentials of the a_1n and $a_2\pi$ orbitals, respectively.[7,9-11,18] The β value of band peak (I) or (II) largely deviates from that for the a_1n band (≈0.2) and is nearly equal to the value for the $a_2\pi$ band. This indicates that IP (I) in Table 1 corresponds to the vertical ionization potential of the $a_2\pi$ band. The vertical ionization potential of the a_1n band may be smaller than IP (I) although it can not be decided precisely on account of the overlap of the bands.

We can see from Fig. 1 and Table 1 that the β values of the third bands of pyridine and 2,6-lutidine are ≈0.8 and ≈0.7, respectively, and are nearly equal to each other. This supports Heilbronner and co-workers' assignments of the third bands of pyridine and 2,6-lutidine.[7,9-11]

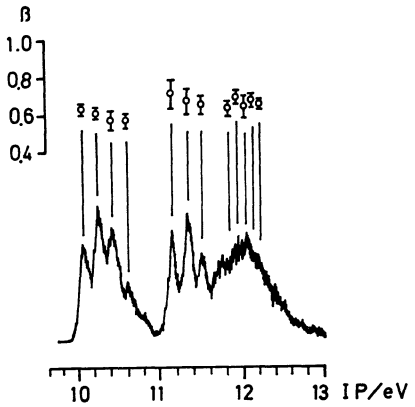

Fig. 2. The first, second, and third bands of the photoelectron spectrum of pentafluoropyridine and their β values.

The first three bands of the photoelectron spectrum of pentafluoropyridine are shown in Fig. 2 and the β values in Table 1 are also plotted against IP in Fig. 2. Brundle and co-workers assigned the first, second, and

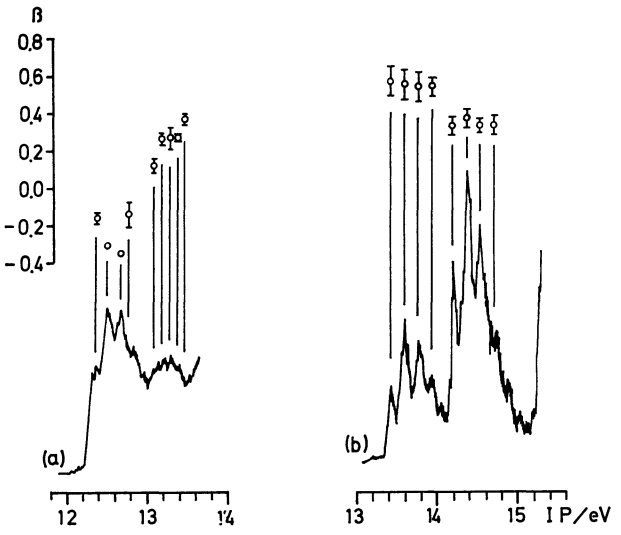

Fig. 3. The fourth and fifth bands of the photoelectron spectra of pyridine (a) and pentafluoropyridine (b) and their β values.

third bands to the $a_2\pi$, $b_1\pi$, and a_1n orbitals, respectively.[18] As is seen in Fig. 2 and Table 1, the β values of the $a_2\pi$ and $b_1\pi$ bands are $\approx$0.6 and $\approx$0.7, respectively. These values are nearly equal to those of the corresponding bands of pyridine, respectively. This also supports the above assignments. The β value ($\approx$0.6) of the a_1n band of pentafluoropyridine, however, differs largely from that ($\approx$0.2) of the corresponding a_1n band of pyridine (see Figs. 1(a), 2, and Table 1). This suggests that the character of the a_1n orbital of pyridine has been considerably changed by the perfluorination.

The fourth and fifth bands of the photoelectron spectra of pyridine and pentafluoropyridine are shown in Figs. 3(a) and (b), respectively, and the β values in Table 1 are also plotted against IP in Fig. 3. Brundle and co-workers assigned the fifth band of pyridine and the fourth band of pentafluoropyridine to the lowest occupied $b_1\pi$ orbitals and the fourth band of pyridine and the fifth band of pentafluoropyridine to the $b_2\sigma$ orbitals mainly from the perfluoro effect.[18] The result of our angular distribution measurements supports this assignment as described below.

The β value of the $b_1\pi$ band (fourth band) of pentafluoropyridine is $\approx$0.6 while the β values of the fourth and fifth bands of pyridine are -0.14——-0.35 and 0.12—0.37, respectively. Comparing these β values, the $b_1\pi$ band of pentafluoropyridine should be correlated with not the fourth band but the fifth band of pyridine. Therefore, the fifth band of pyridine is assigned to the lowest occupied $b_1\pi$ orbital. The fourth band of pyridine is necessarily assigned to the $b_2\sigma$ orbital.

We can see that the β value of the $b_2\sigma$ band of pyridine is largely different from that of pentafluoropyridine (see Fig. 3 and Table 1). This indicates that the character of the $b_2\sigma$ orbital of pyridine has been changed by the perfluorination.

In conclusion, the five lower-energy bands of the photoelectron spectrum of pyridine can be assigned to the a_1n, $a_2\pi$, $b_1\pi$, $b_2\sigma$, and $b_1\pi$ orbitals from the lower IP side, respectively, and it is found that the β values of the a_1n and $b_2\sigma$ bands of pyridine are considerably changed by perfluorination while those of the π bands of pyridine are scarcely changed by it.

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