Chemistry of Excited States. Part 13.† Assignment of Lowest π-Ionizations in Photoelectron Spectra of Thiophen, Furan, and Pyrrole

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An assignment of the lowest π-ionizations($1b_1\pi$) in thiophen, furan, and pyrrole at 12.5, 15.3, and 12.9 eV, respectively, is achieved by a comparison of observed He^{II}/He^{I} intensity changes in the corresponding photoelectron spectra with calculated intensity trends for different possible assignments.

THIOPHEN, furan, and pyrrole are among the most important constituent parts of heterocyclic compounds. This also explains the large number of papers dealing with the elucidation of their electronic structure by means of photoelectron (p.e.) spectroscopy[1-9] often in conjunction with various types of quantum chemical calculations found in the literature.[2,4,8-21] Although the outer valence region (ionization energies $E_i < 15$—16 eV) in the p.e. spectra has been widely investigated, there are still discrepancies concerning the sequence of σ-orbitals (a_1,b_2) and the assignment of the lowest π-orbital ($1b_1\pi$) in these molecules.

In a previous paper[22] we reported the assignment of the lowest π-orbital ionization in the p.e. spectrum of pyridine *N*-oxide based on the He^{II}/He^{I} intensity comparison. We report here a similar study of thiophen, furan, and pyrrole where we have taken into account additionally calculated relative intensities and the results of various quantum chemical calculations.

EXPERIMENTAL AND CALCULATIONS

The p.e. spectra of thiophen, furan, and pyrrole were recorded on a Vacuum Generators UV-G3 spectrometer which enables good determination of He^{II}/He^{I} intensity changes over the whole region.[23] The relative intensity (I_r) of a band system i corresponds to its area normalized to the area of the first band system and corrected by a factor f_i [equation (1); S_1 and S_i describe the sensitivity of the

$$f_i = \frac{S_1}{S_i} \simeq \frac{E_k(i)}{E_k(1)} \qquad (1)$$

analyser (an energy-dependent parameter of the spectrometer) for the first and ith band system, respectively, and $E_k(1)$ and $E_k(i)$ the corresponding kinetic energy of the photo-electrons].

According to Siegbahn[24] the theoretical photoionization cross-section, σ_i^{MO}, for different excitation energies for the ith MO can be determined from populations and the photoionization cross-section of the basis orbitals σ_μ^{AO} [equation (2)]. Equation (2) has been extensively tested[25]

$$\sigma_i^{MO} = \sum_{\mu,\ \text{all atoms}} \sigma_\mu^{AO} \,.\, P_{i\mu} \qquad (2)$$

by investigating the intensity changes on going from He^{I} to He^{II} excitation. In the present work the $\sigma_\mu'^{AO}$ values were determined according to the method of Schweig *et al.*[26] However, as shown in refs. 27 and 28, the σ_i^{MO} in (2) correspond only to the inclusion of one-centre contributions.‡

The $P_{i\mu}$ values were determined from a wave function calculated by spectroscopically adjusted INDO-type calculations (INDO/RZ).[29-31] The experimental molecular geometries for thiophen,[32] furan,[33] and pyrrole[34] were used in the calculations. All ionization energies in the investigated region were also calculated by a doublet-LCI (limited-CI) procedure[35] based on the INDO/RZ method, since there is no *a priori* certainty that a satisfactory description, both qualitatively and quantitatively, of the p.e. band system can be achieved by assigning them to a single MO (or only one Koopmans' configuration).[35-37] This condition, however, has to be fulfilled before the intensity model used here can be applied.

The different sets of figures for each molecule representing the calculated He^{II}/He^{I} relative intensity ratios of individual band systems for different assignments, He^{II}/He^{I} (calc), were compared with the set of observed ratios, He^{II}/He^{I} (exp), using the agreement index (3) (as suggested by one of the referees).

$$R = \frac{\Sigma|He^{II}/He^{I}\ (\text{exp}) - He^{II}/He^{I}\ (\text{calc})|}{\Sigma He^{II}/He^{I}\ (\text{exp})} \,.\, 100 \qquad (3)$$

The use of this index (see Tables 1—3) gives results in agreement with the conclusions reached in this study, *i.e.* clearly favours the proposed assignments.

RESULTS AND DISCUSSION

Thiophen.—The He^{I} and He^{II} p.e. spectra of thiophen are shown in Figure 1. In the region $E_i < 15$ eV seven band systems can be identified which have been assigned in the literature as follows:

I Derrick *et al.*[2]

$a_2\pi < b_1\pi < b_1\pi < \sigma$

II Gelius *et al.*[5]

$a_2\pi < b_1\pi < a_1n < b_2 < b_1\pi < a_1 < b_2$

III von Niessen *et al.*[20]

$a_2\pi < b_1\pi < a_1n < b_1\pi < b_2 < a_1 < b_2$

IV Sell *et al.*[38]

$a_2\pi < b_1\pi < a_1n < b_1\pi < \sigma$

V de Alti *et al.*[39]

$a_2\pi < b_1\pi < b_1\pi < a_1n < b_2 < a_1 < b_2$

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† Part 12, M. Scholz, *J. Prakt. Chem.*, in the press.

‡ The choice of σ_μ^{AO} is, in the present case of low-energy photoelectrons, generally dubious.[25] Changes in relative He^{II}–He^{I} band intensities should be, however, correctly reproduced on the basis of σ_μ^{AO} used here.[27,28]

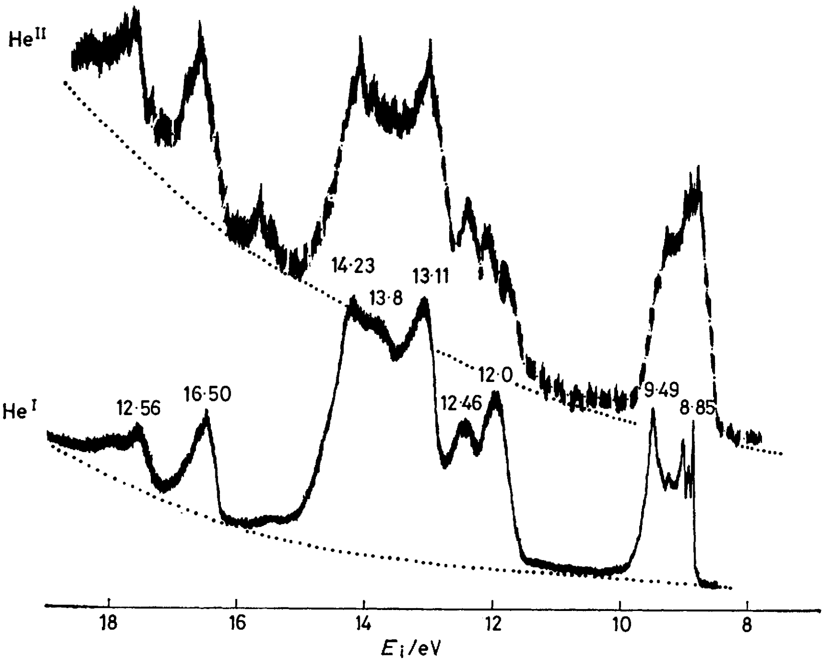

FIGURE 1 The He^{I} and He^{II} p.e. spectra of thiophen. The corresponding base lines are indicated by dotted lines. Vertical ionization energies E_i (in eV) are given above the systems in the He^{I} spectrum

The assignments differ only in the location of the lowest $b_1\pi$ orbital. The result (I) was obtained semiempirically by comparison of the lowest π-systems in benzene and furan spectra with calculated MO energies (EHT). The assignment III corresponds to *ab initio* orbital energies (ε_i^{HF}) corrected for reorganization and correlation effects by the many-body-Green-function (MBGF) method. However, this correction did not change the orbital sequence given by the Koopmans' theorem.[20] In IV Sell *et al.*,[38] measuring the angular distribution of photoelectrons and determining the asymmetry parameter β, which in a characteristic way differs for π- and σ-systems, found the same sequence as III. The result V was obtained by MS SCF Xα calculations. Assignment II is based on the simulation of ESCA band intensities using an approach similar to equation (2) and an orbital sequence given by Gelius *et al.*[15] which differs from the *ab initio* result.[20] Assignment I was found to be less probable than II, whereas III was not considered.

TABLE 1

Comparison of experimental *versus* calculated data and assignment of the p.e. spectrum of thiophen

	Experimental				Calculated						
		Relative intensity			Ratio He^{II}/He^{I} for different assignments				Ionization energy [a] E_i/eV		
System	Ionization energy E_i/eV	He^{I}	He^{II}	Ratio He^{II}/He^{I}	I[2]	II[5]	III[20]	IV[38]	KT [b]	CI [c]	Present assignment
1	8.85	1.00	1.00	1.00	1.00	1.00	1.00	1.00	8.5	8.2 (97% $1a_2^{-1}$)	$1a_2\pi$
2	9.49	1.05	0.85	0.81	0.73	0.73	0.73	0.73	9.8	10.1 (92% $2b_1^{-1}$)	$2b_1\pi$
3	12.00	1.05	0.50	0.48	1.04	0.76	0.76	0.76	12.0	12.2 (96% $6a_1^{-1}$)	$6a_1$n
4	12.46	0.75	0.65	0.87		0.85	1.11	1.11	13.2	13.0 (78% $1b_1^{-1}$)	$1b_1\pi$
5	13.11	1.60	1.25	0.78		1.21	0.90		13.1	13.2 (91% $4b_2^{-1}$)	$4b_2$
6, 7	13.80	2.90	2.45	0.84		0.97	0.97		14.5	14.3 (87% $5a_1^{-1}$)	$5a_1$
	14.23								13.9	13.8 (87% $3b_2^{-1}$)	$3b_2$
	Agreement index R					20%	18%				

[a] INDO/RZ. [b] Koopmans' theorem only. [c] Configuration interaction (152 configurations).

The present observed and calculated changes of relative intensities on going from He^{I} to He^{II} excitation are given as ratios I_r (He^{II})/I_r (He^{I}) denoted by He^{II}/He^{I} for assignments I—IV in Table 1. The strong decrease of the relative intensity of He^{II} of the third system excludes the assignments I and V as correct. Less significant for the identification of the lowest π-orbital are He^{II}/He^{I} intensity ratios of systems 4—7. The trend of calculated intensity changes, however, favours the assignment(s) III (and IV) over II. Thus, the ionization of the $1b_1\pi$ orbital should correspond to the system at 12.46 eV in the He^{I} p.e. spectrum of thiophen.

The ionization energies E_i calculated in the INDO/RZ formalism applying both Koopmans' theorem and the doublet-LCI method are given in Table 1. The inclusion of configuration interaction effects between Koopmans' and non-Koopmans' configurations does not change the ordering obtained by single configuration interpretation in the given region of the spectrum. The many-determinant approach and the inclusion of the reorganization effect, however, result in an interchange of $4b_2$ and $1b_1\pi$ in comparison with the orbital sequence given by Koopmans' theorem.

Furan.—In the furan p.e. spectrum (Figure 2) in the region of ionization energies $E_i < 16$ eV six clearly separated peaks are observed, which usually were assigned to seven MOs:

I Derrick *et al.*[2]

$$a_2\pi < b_1\pi < a_1n < b_2 < b_1\pi < \{a_1 < b_2\}$$

II Gelius *et al.*[5]
von Niessen *et al.*[20]

$$a_2\pi < b_1\pi < a_1n < a_1 < b_2 < \{b_2 < b_1\pi\}$$

III Sell *et al.*[38]

$$a_2\pi < b_1\pi < \sigma < \sigma < \sigma < \{\sigma < \sigma\} < b_1\pi$$

IV de Alti *et al.*[39]

$$a_2\pi < b_1\pi < a_1n < a_1 < b_1\pi < b_2 < b_2$$

V Åsbrink *et al.*[40]

$$a_2\pi < b_1\pi < a_1n < b_2 < a_1 < \{b_1\pi < b_2\}$$

The assignments I—IV were obtained in the same manner as described for thiophen. The results V are from a HAM/3 [41] calculation.

For furan there are also considerable discrepancies concerning the assignment of the lowest π-orbital: 14.5 eV (I,IV), between 15 and 16 eV (II,V), 17.5 eV (III). Table 2, analogously to Table 1, displays the observed and calculated intensity changes (He^{II}/He^{I}) for different assignments. The trend of intensity change is best reproduced by II, however, similarly as in thiophen, with too high a He^{II}/He^{I} ratio for the σ-lone pair MO(a_1n).

The assignment of the lowest $b_1\pi$ orbital to the system at 14.5 eV [2,39] is practically impossible [He^{II}/He^{I} (calculated) = 2.71!], but to systems 6 or 7 is very probable, since both, experimentally and theoretically, give a strong rise in the relative intensity of the band system in the He^{II} spectrum. Even for system 8 the intensity increases considerably. However, the currently most reliable procedures for the interpretation of valence electron photoionization spectra of organic molecules (MBGF method, HAM/3) yield ionization energies for the lowest π-orbital which considerably (>2 eV) differ from the energy of system 8 (see Table 2). This deviation is out of the range of error usually assumed for both procedures. From the results of the CI-calculation shown in Table 2, it can be seen that the p.e. systems in the investigated range of the spectrum are satisfactorily described by a single Koopmans' configuration.

Pyrrole.—The He^{I} and He^{II} spectra of pyrrole are shown in Figure 3. The seven systems of $E_i < 15$ are ascribed in the literature to the following seven MOs:

I Derrick *et al.*[2]
Åsbrink *et al.*[40]

$$a_2\pi < b_1\pi < \{a_1 < b_1\pi\} < b_2 < a_1 < b_2$$

II Gelius *et al.*[5]

$$a_2\pi < b_1\pi < \{a_1 < b_2\} < b_2 < b_1\pi < a_1$$

III von Niessen *et al.*[21]

$$a_2\pi < b_1\pi < \{a_1 < b_2\} < b_1\pi < b_2 < a_1$$

IV Tanaka *et al.*[42]

$$a_2\pi < b_1\pi < \{b_1\pi,\sigma\} < \sigma$$

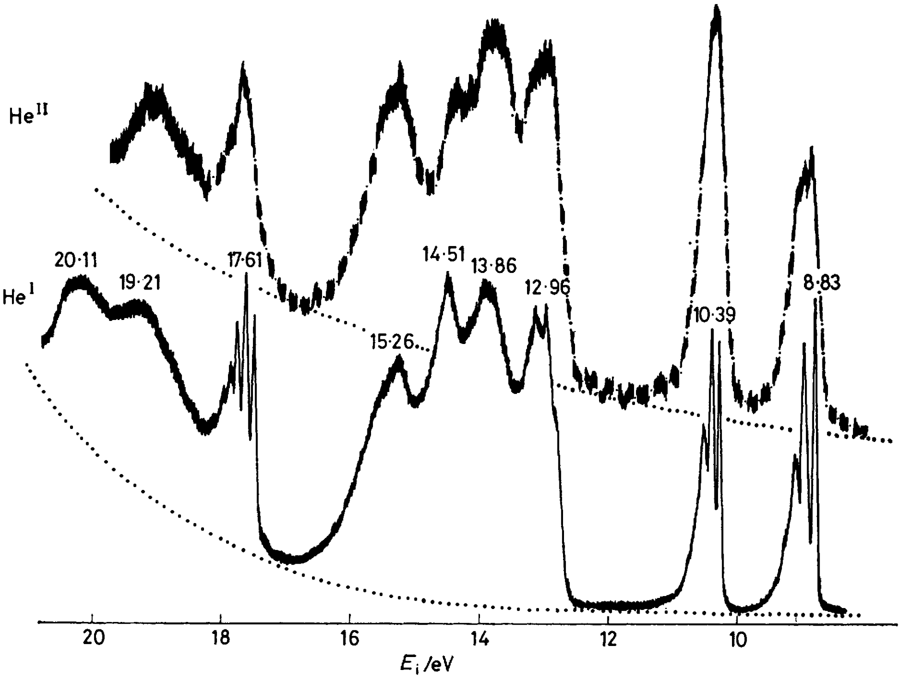

FIGURE 2 The He^{I} and He^{II} p.e. spectra of furan. The corresponding base lines are indicated by dotted lines. Vertical ionization energies E_i (in eV) are given above the systems in the He^{I} spectrum

The assignment IV is made on the basis of an *ab initio*-CI calculation for the ground and excited states of pyrrole and its radical cation (for I—III see thiophen and furan). Table 3, analogously to the previous examples, contains the intensity data for the first seven systems of pyrrole. It is easy to see that a clear identification of the lowest π-orbital is hardly possible on the basis of the observed intensity changes only, because of the very small changes for systems 3—7. Similarly, in a recently published angular dependence study,[38] only the first two systems yielded an asymmetry parameter β typical for π-ionizations. Therefore, the third π-system was impossible to assign. The small intensity changes favour mostly the assignment I (or IV), since in all other cases, contrary to the observation, a rise of the π-system upon He$^{\text{II}}$ excitation is expected (He$^{\text{II}}$/He$^{\text{I}}$ = 2.19 for II and 2.0 for III).

TABLE 2

Comparison of experimental *versus* calculated data and assignment of the p.e. spectrum of furan

	Experimental				Calculated								
		Relative intensity			Ratio He$^{\text{II}}$/He$^{\text{I}}$ for different assignments				Ionization energy E_i/eV				
System	Ionization energy E_i/eV	He$^{\text{I}}$	He$^{\text{II}}$	Ratio He$^{\text{II}}$/He$^{\text{I}}$	I[2]	II[5]	III[38]	V[41]	MBGF[a]	HAM/3[b]	KT[c]	CI[d]	Present assignment
1	8.83	1.00	1.00	1.00	1.00	1.00	1.00	1.00	8.9	9.4	8.5	8.3 (98% $1a_2^{-1}$)	$1a_1\pi$
2	10.39	0.85	1.20	1.41	1.22	1.22	1.22	1.22	10.4	10.7	10.8	10.6 (95% $2b_1^{-1}$)	$2b_1\pi$
3	12.96	1.25	1.25	1.00	1.43	1.43	1.43	1.43	13.3	13.2	13.9	13.9 (75% $6a_1^{-1}$ + 20% $5a_1^{-1}$)	$6a_1$n
4	13.86	1.40	1.55	1.11	0.95	1.11		0.95	14.1	14.7	14.3	14.1 (69% $5a_1^{-1}$ + 21% $6a_1^{-1}$)	$5a_1$
5	14.51	1.00	0.90	0.90	2.71	1.02		1.20	14.7	14.5	13.8	13.7 (96% $4b_2^{-1}$)	$4b_2$
6, 7	15.26	1.00	1.75	1.75	1.10	1.43	1.10	1.43	15.5	15.5	16.2	15.9 (64% $1b_1^{-1}$)	$1b_1\pi$
	15.26								15.2	15.7	16.5	16.3 (77% $3b_2^{-1}$)	$3b_2$
	Agreement index R				45%	15%		20%					

[a] Ref. 20. [b] Ref. 40. [c] INDO/RZ Koopmans' theorem only. [d] INDO/RZ-LCI (152 configurations).

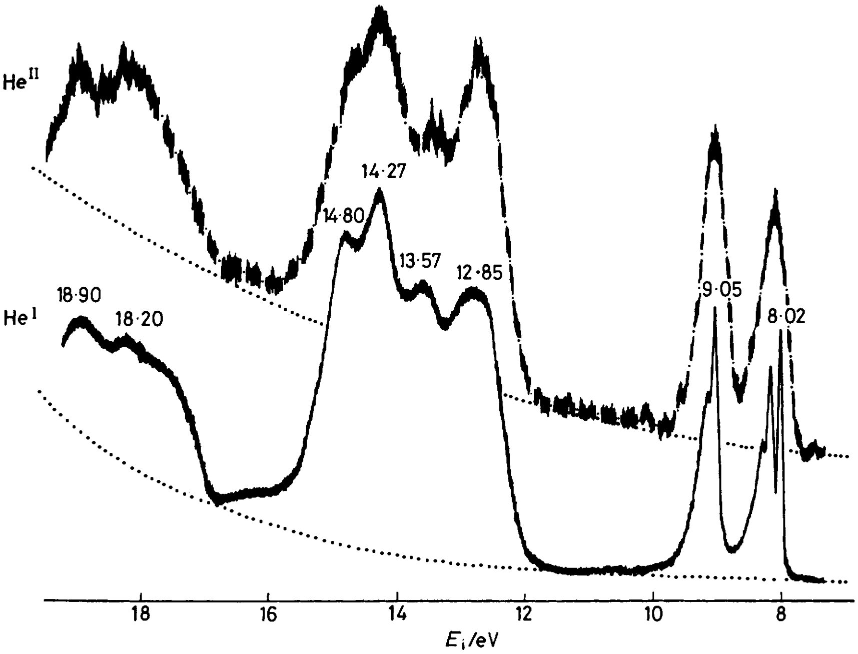

FIGURE 3 The He$^{\text{I}}$ and He$^{\text{II}}$ p.e. spectra of pyrrole. The corresponding base lines are indicated by dotted lines. Vertical ionization energies E_i (in eV) are given above the systems in the He$^{\text{I}}$ spectrum

The inclusion of the configurational interaction effect yields an explanation for the difficulties in the experimental assignment of the $1b_1\pi$-orbital. Namely, the application of the intensity model becomes critical, since the low purity of the $^2B_1$-configuration (40 and 47%,[42] respectively, Table 3) arising from mixing with shake-up configurations (breakdown of the orbital interpretation) results in a lower relative intensity of the system. Therefore, probability statements on the basis of explicitly calculated ionization energies (Table 3) should always be part of the procedure of making a 'correct' assignment.

The present assignment of the lowest π-orbital to the overlapping systems in the region of 13 eV made on the basis of intensity comparison is supported by the HAM/3 [40] and CI-calculation [42] but is in disagreement with the sequence given by von Niessen *et al.*[21]

The $^2B_1$ configuration, in comparison with the $1b_1\pi$-orbital, is considerably shifted to lower ionization energies as a result of strong configuration interaction (*ca.* 1 eV according to INDO/RZ-LCI, *ca.* 2.3 eV according to Tanaka *et al.*[42]). This shift is much stronger than that calculated for the neighbouring σ-orbitals. However, in

TABLE 3

Comparison of experimental *versus* calculated data and assignment of the p.e. spectrum of pyrrole

	Experimental				Calculated									
		Relative intensity			Ratio HeII/HeI for different assignments				Ionization energy E_i/eV					
System	Ionization energy E_i/eV	HeI	HeII	Ratio HeII/HeI	I[2]	II[5]	III[21]	IV[42]	MBGF[a]	HAM/3[b]	KT[c]	CI[d]	CI *ab initio*[e]	Present assignment
1	8.02	1.00	1.00	1.00	1.00	1.00	1.00	1.00	8.2	8.8	8.0	7.8 (97% $1a_2^{-1}$)	8.1 (92%)	$1a_2\pi$
2	9.05	0.95	1.15	1.21	1.29	1.29	1.29	1.29	8.9	9.8	9.4	9.3 (91% $2b_1^{-1}$)	8.9 (89%)	$2b_1\pi$
3, 4	12.85								13.0	13.1	13.8	13.6 (84% $6a_1^{-1}$)		$6a_1$
		1.85	1.70	0.92	1.47	1.12	1.12	1.47					13.3 (47%)	
	12.85								13.7	13.5	14.9	14.0 (40% $1b_1^{-1}$)		$1b_1\pi$
5	13.57	1.15	0.85	0.74	1.09	1.09	2.00		13 4	13.8	13.4	13.4 (95% $4b_2^{-1}$)		$4b_2$
6	14.27	1.50	1.65	1.10	1.37	2.19	1.21		14.9	14.6	15.2	15.3 (86% $5a_1^{-1}$)		$5a_1$
7	14.80	1.15	1.05	0.91	1.31	1.55	1.55		14.4	14.9	15.6	15.5 (89% $3b_2^{-1}$)		$3b_2$
	Agreement index *R*				28%	40%	39%							

[a] Ref. 21. [b] Ref. 40. [c] INDO/RZ Koopmans' theorem only. [d] INDO/RZ-LCI (152 configurations). [e] Ref. 42.

the case of INDO/RZ-LCI calculations this does not yield to a change of the sequence predicted by Koopmans' theorem, probably because of the strongly limited configuration set. A final clarification of this problem seems achievable only by large-scale non-empirical CI-studies, taking into consideration all ionic states in the corresponding energy region.

Conclusions.—The present investigation indicates that the HeII/HeI intensity comparison enables the assignment of valence shell p.e. spectra of organic molecules not only in cases when the ionic states of different symmetry (σ,π) exhibit remarkable changes in spectral intensities (*e.g.* ref. 22 and furan $1b_1\pi$-state) but also in less pronounced examples (thiophen, pyrrole) when it can be used in conjunction with calculated intensity trends to enable a choice between different possible assignments. It is important to point out here that the reliability of calculated values should be checked first by comparison of the energies over the whole p.e. spectrum. Secondly, one has to make sure that a one-configuration interpretation (MO interpretation) is satisfactory, *i.e.* that its contribution remains dominant even when CI is allowed for. The necessity of such a test is evident in the case of the lowest $b_1\pi$-system of pyrrole, giving an explanation for the discrepancies in its assignment.

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REFERENCES

[1] J. H. D. Eland, *Int. J. Mass Spectrom. Ion Phys.*, 1969, **2**, 471.

[2] P. J. Derrick, L. Åsbrink, O. Edqvist, B. Ö. Jonsson, and E. Lindholm, *Int. J. Mass Spectrom. Ion Phys.*, 1971, **6**, 161, 177, 191.

[3] P. J. Derrick, L. Åsbrink, O. Edqvist, and E. Lindholm, *Spectrochim. Acta*, 1971, **27A**, 2525.

[4] M. J. S. Dewar, A. J. Harget, N. Trinajstić, and S. D. Worley, *Tetrahedron*, 1970, **26**, 4505.

[5] U. Gelius, C. J. Allan, G. Johansson, H. Siegbahn, D. A. Allison, and K. Siegbahn, *Phys. Scr.*, 1971, **3**, 237.

[6] G. Distefano, S. Pignataro, G. Innorta, F. Fringuelli, G. Marino, and A. Taticchi, *Chem. Phys. Lett.*, 1973, **22**, 132.

[7] W. Schäfer, A. Schweig, S. Gronowitz, A. Taticchi, and F. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 1973, 541.

[8] Z. Božić, K. Humski, T. Cvitaš, and L. Klasinc, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1413.

[9] V. Galasso, L. Klasinc, A. Sabljić, N. Trinajstić, G. C. Pappalardo, and W. Steglich, *J. Chem. Soc., Perkin Trans. 2*, 1981, 127.

[10] E. Clementi, H. Clementi, and D. R. Davis, *J. Chem. Phys.*, 1967, **46**, 4725.

[11] D. T. Clark, *Tetrahedron*, 1968, **24**, 2663, 3285, 4686.

[12] B. Mely and A. Pullman, *Theor. Chim. Acta*, 1969, **13**, 278.

[13] P. Siegbahn, *Chem. Phys. Lett.*, 1971, **8**, 245.

[14] M. H. Palmer, A. J. Gaskell, and M. S. Barber, *Theor. Chim. Acta*, 1971, **23**, 52; 1972, **26**, 357.

[15] U. Gelius, B. Roos, and P. Siegbahn, *Theor. Chim. Acta*, 1972, **27**, 171.

[16] D. W. Genson and R. E. Christoffersen, *J. Am. Chem. Soc.*, 1972, **94**, 6904.

[17] J. P. Dahl and A. E. Hansen, *Theor. Chim. Acta*, 1963, **1**, 199.

[18] J. J. Kaufman, H. J. T. Preston, E. Kerman, and L. C. Cusachs, *Int. J. Quantum Chem. Symp.*, 1973, **7**, 249.

[19] H. J. T. Preston and J. J. Kaufman, *Int. J. Quantum Chem. Symp.*, 1973, **7**, 207.

[20] W. von Niessen, W. P. Kraemer, and L. S. Cederbaum, *J. Electron Spectrosc.*, 1976, **8**, 179.

[21] W. von Niessen, L. S. Cederbaum, and G. H. F. Diercksen, *J. Am. Chem. Soc.*, 1976, **98**, 2066.

[22] L. Klasinc, I. Novak, G. Kluge, and M. Scholz, *Z. Naturforsch., Teil. A*, 1980, **35**, 640.

[23] L. Klasinc, B. Kovač, and B. Ruščić, *Kem. Ind.* (*Zagreb*), 1974, **23**, 569.

[24] K. Siegbahn, *J. Electron Spectrosc.*, 1974, **5**, 3.

[25] V. G. Yarzhemsky, V. I. Nefedov, M. Ya. Amusia, N. A. Cherepkov, and L. V. Chernysheva, *J. Electron Spectrosc.*, 1980, **19**, 123.

[26] A. Schweig and W. Thiel, *J. Chem. Phys.*, 1974, **60**, 951.

[27] A. Schweig and W. Thiel, *J. Electron Spectrosc.*, 1973, **2**, 199.

[28] A. Schweig and W. Thiel, *Mol. Phys.*, 1974, **27**, 265.

[29] J. Ridley and M. Zerner, *Theor. Chim. Acta*, 1973, **32**, 111.

[30] J. Ridley and M. Zerner, *Theor. Chim. Acta*, 1976, **42**, 223.

[31] G. Kluge and M. Scholz, *Z. Chem.*, 1979, **19**, 457.

[32] B. Bak, D. Christensen, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Mol. Spectrosc.*, 1961, **7**, 58.

[33] B. Bak, L. Hansen, and J. Rastrup-Andersen, *Discuss. Faraday Soc.*, 1955, **19**, 30.

[34] L. Hansen-Nygaard, J. T. Nielsen, J. Kircheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sorensen, *J. Mol. Struct.*, 1969, **3**, 491.

[35] G. Kluge and M. Scholz, *Int. J. Quantum Chem.*, 1981, **20**, 669.

[36] L. S. Cederbaum, W. Domcke, J. Schirmer, W. von Niessen, G. H. F. Diercksen, and W. P. Kraemer, *J. Chem. Phys.*, 1978, **69**, 1591.

[37] W. von Niessen, W. P. Kraemer, and G. H. F. Diercksen, *Chem. Phys.*, 1979, **41**, 113.

[38] J. A. Sell and A. Kuppermann, *Chem. Phys. Lett.*, 1979, **61**, 355.

[39] G. de Alti and P. Decleva, *Chem. Phys. Lett.*, 1981, **77**, 413.

[40] L. Åsbrink, C. Fridh, and E. Lindholm, *J. Electron Spectrosc.*, 1979, **16**, 65.

[41] L. Åsbrink, C. Fridh, and C. Lindholm, *Chem. Phys. Lett.*, 1977, **52**, 63, 69; HAM/3 program from QCPE 393 (1980).

[42] K. Tanaka, T. Nomura, T. Noro, H. Tatewaki, T. Takeda, H. Kashiwagi, F. Sasaki, and K. Ohno, *J. Chem. Phys.*, 1978, **67**, 5738.