

## A Study of the He(I) and He(II) Intensity Ratios of a Series of Substituted Pyridines (Pyridine, Pentafluoro-, 2-Fluoro-, 2-Methyl, 2-Cyano-, 2-Aminopyridine and Pyrazine)

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Received August 8, 1977

*Within a closely related series of substituted pyridines a similar behaviour of the He(I)/He(II) intensity ratio of bands originating from the same type of orbital is discussed qualitatively. Starting from compounds that have been unambiguously interpreted, empirical rules concerning the behaviour of the intensity could be set up. In other less clear cases the spectra could be interpreted using these rules.*

### Introduction

Studying the photoelectron spectra of transition metal complexes with N donor ligands we noticed some assignment problems and contradictions in the literature. For the assignments of photoelectron bands several criteria are used.

Semi-empirical or *ab initio* calculations, together with Koopman's theorem, have often been related to the band positions [1]. Sometimes the band shape has been related to the bonding-, anti-bonding or non-bonding character of the orbital. Additionally, fine structure in the spectra, originating from vibrations in the ionic state, could be observed giving decisive information concerning the assignments [2]. Within a closely related series of compounds substituent effects and especially the perfluoro effect may give important indications about the electron density distribution in the molecule [3]. Relative intensities, *i.e.* differential cross sections may be of help in the assignment problems by the degeneracy of the ionized molecular orbitals, this being proportional to the intensity of the band to a first approximation [4]. The comparison of the relative intensities of the bands with respect to the incident photon energy, *viz.* for He(I) and He(II) spectra, provides us with a new useful assignment criterion. In this paper we report the applicability of this criterion on a series of N-donor ligands.

### Experimental

The spectra were recorded on a Perkin–Elmer P.S.-18 photospectrometer modified with a Helectros He(I)–He(II) source. The compounds pyridine, pentafluoro-, 2-methyl-, 2-cyano-, 2-aminopyridine and pyrazine, were commercially available and purified in the usual manner; 2-fluoropyridine was synthesized and purified by standard methods [5].

### Determination of the Band Intensities

The spectrometer contains an electrostatic 127° deflection analyzer. The collecting efficiency of this analyzer is proportional to the initial electron kinetic energy to a first order approximation [6]. In order to correct for this analyzer effect, the peak areas were divided by the initial electron kinetic energy corresponding to the vertical transition of the band. Only if peaks were sufficiently separated was a quantitative treatment possible. Otherwise a qualitative estimate could often be made by a direct comparison of the He(I) and He(II) spectra without the kinetic energy correction.

The construction of the apparatus allows only electrons ejected perpendicular to the photon beam to reach the detector, so that the corrected peak areas are a measure of the differential cross section at a right angle to the beam. The fundamental expression for the differential cross section  $d\sigma_n$  for producing photoelectrons represented by an orthogonalized plane wave at solid angle  $d\Omega$  and with  $\Omega$  normal to the incident photon beam is [7–9]:

$$\frac{d\sigma_n}{d\Omega} \propto k_n |\mu P_{on}|^2$$

In this expression the differential cross section shows a direct dependence with the photoelectron energy by

$$k_n = \frac{2m_e}{h} (\hbar\omega - I_n)^{1/2}$$

All the measured peak areas were also corrected for the  $k_n$  factor, so that the resultant values are directly

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TABLE I. Ionization Potentials (in eV) and Assignment of the P.e. Spectra of Some Substituted Pyridines.

Pyridine	9.67-lpN(a <sub>1</sub> )	9.79-π(a <sub>2</sub> )	10.51-π(b <sub>1</sub> )	
Pentafluoropyridine	10.27-π(a <sub>2</sub> )	11.37-π(b <sub>1</sub> )	12.08-lp(a <sub>1</sub> )	
2-Fluoropyridine	9.85-π <sub>3</sub>	10.45-lpN	10.85-π <sub>2</sub>	
α-Picoline	9.25-π <sub>3</sub>	9.39-lpN	10.29-π <sub>2</sub>	
2-Cyanopyridine	10.12-π <sub>3</sub>	10.42-lpN	11.10-π <sub>2</sub>	
2-Aminopyridine	8.34-π <sub>4</sub>	9.57-lpN	10.15-π <sub>3</sub>	11.16-π <sub>2</sub>
Pyrazine	9.63-lpN(A <sub>g</sub> )	10.18-π(b <sub>2g</sub> )	11.35-lpN(b <sub>2u</sub> )	11.77-π(b <sub>1u</sub> )

TABLE II. Increase of the Bands Intensity Ratio From He(I) to He(II) Relative to the He(I) Intensity (%).<sup>a,b</sup>

Pyridine	- 3-lpN(a <sub>1</sub> ) + π(a <sub>2</sub> )		+ 7-π(b <sub>1</sub> )	
Pentafluoropyridine	+ 3-π(a <sub>2</sub> )	+12-π(b <sub>1</sub> )	-14-lpN(a <sub>1</sub> )	
2 Fluoropyridine	-18-π <sub>3</sub>	+ 2-lpN	+ 9-π <sub>2</sub>	
α-Picoline	- 2-lpN + π <sub>3</sub>		+ 4-π <sub>2</sub>	
2-Cyanopyridine	- 3-lpN + π <sub>3</sub>		+ 6-π <sub>2</sub>	
2 Aminopyridine	+ 3-π <sub>4</sub>	0-lpN	- 7-π <sub>3</sub>	+ 6-π <sub>2</sub>
Pyrazine	-16-lpN(a <sub>g</sub> )	0π(b <sub>2g</sub> )	0-lpN(b <sub>2u</sub> )	+19-π(b <sub>1g</sub> )

<sup>a</sup>Orbital assignment added in the column. <sup>b</sup>Intensity ratio of a band n is:  $A_n/\sum_j A_j$ ,  $A_n$  is the area of the band n corrected for the photoelectron energy by a factor  $(\hbar\omega - I_{v,n})^{-3/2}$ .

proportional to  $|\mu P_{on}|^2$ , the expectation value of the differential dipole transition moments. This includes both the spherical and the angular contributions of the photoelectron. In principle, both variables may vary on changing the energy of the photon beam. It is essential in this approach that a similar behaviour of the  $|\mu P_{on}|^2$  parameter exists throughout the whole series of compounds. Thus only one type of orbital may be compared in closely related molecules and assigned with respect to intensity differences.

Since no absolute value of  $|\mu P_{on}|^2$  can be measured, we have calculated the ratio of the peak area relative to all bands concerned and corrected for the photoelectron energies as mentioned before. The increase of this ratio on going from He(I) to He(II) relative to the ratio in He(I) is tabulated in Table II. The proposed assignments together with the vertical ionization potentials are listed in Table I.

### Assignments

For pyridine especially some controversy exists about the relative order of the lone pair nitrogen and the two highest π-orbitals. The relative intensity of the first two bands and the doublet character of the first one is evidence that there are two orbitals very close in energy [10]. The perfluoro effect showed that the first band consists of a σ-orbital (lone pair nitrogen) and a π-orbital. The second band must be

π in character [11]. However, the near degeneracy of the two highest orbitals made an unambiguous assignment of the n- and π<sub>3</sub>-orbital impossible. The various calculations contradict each other with respect to the relative order. From a series of fluoro substituted pyridines and the use of substituent parameters it was concluded that the relative order in pyridine should be π(a<sub>2</sub>), n, π(b<sub>1</sub>) [12]. This was, however, contradicted by a similar article comparing methyl, tertiary butyl and trimethylsilyl substituted pyridines [13]. In pentafluoropyridine, the assignment of the three highest bands is unambiguous: π(a<sub>2</sub>), π(b<sub>1</sub>), n. The relative position of π(a<sub>2</sub>) and π(b<sub>1</sub>) is confirmed by the He(I)-He(II) intensity changes, *i.e.* π(b<sub>1</sub>) increases strongly relative to π(a<sub>2</sub>). A similar behaviour is found for the five membered hetero cycles pyrrole [14] and furan [15]. By analogy with Schweig [16] this can be explained by changes in the spherical contribution, caused by the difference in the electron density on the electronegative nitrogen atom.

For the nitrogen lone pair orbital we notice in Table II a strong decrease in intensity on going from He(I) to He(II). Just as expected, we found a relative intensity increase in the He(II) spectrum for the second band at 10.51 eV for pyridine, assigned as π(b<sub>1</sub>).

The low binding energy side of the first band in pyridine shows a decrease in the He(II) spectrum compared to He(I). This new criterion thus confirms the assignment of Heilbronner *et al.* [13], the highest

orbital being lone pair in character followed by  $\pi(a_2)$  and  $\pi(b_1)$  respectively.

2-fluoropyridine also shows a large intensity difference between the He(I) and He(II) spectra. The accepted orbital order is  $\pi_3, n, \pi_2$  [12]. In considering this molecule as a distorted  $C_{2v}$  system, the  $\pi_3$ -orbital is strongly related to the  $\pi(a_2)$  (with low electron density on N) and  $\pi_2$  to  $\pi(b_1)$  (with high electron density on N). As expected the  $\pi_3$  decreases from He(I) to He(II) with respect to  $\pi_2$ . In contrast to pentafluoropyridine the band assigned to the nitrogen lone pair of 2-fluoropyridine increases in intensity from He(I) to He(II) relative to the  $\pi_3$ -orbital intensity.

Although the lone pair orbital and the  $\pi_3$  in  $\alpha$ -picoline are practically merged into one band, the band shape clearly shows a decrease on the low binding energy side in the He(II) spectrum. Therefore, by analogy to 2-fluoropyridine, the highest occupied orbital must be  $\pi_3$  and the next one a lone pair. Taking the total area of the first band,  $\pi_3$  and lone pair on nitrogen, with respect to the second band,  $\pi_2$ , a relative decrease of the first band for  $\alpha$ -picoline is observed. In the 2-fluoropyridine p.e. spectrum the three bands are clearly separated and the increase of  $\pi_2$  from He(I) to He(II) dominates, so similar to  $\alpha$ -picoline a decrease of  $\pi_3$  and the lone pair on nitrogen is noticed.

An exactly similar situation is found comparing the He(I) and He(II) spectra of 2-cyanopyridine. Using the same arguments this leads to the same relative order of the highest occupied orbitals, i.e.  $\pi_3, n, \pi_2$ , in perfect agreement with assignments based on CNDO/2 calculations [17].

The difference in behaviour of the lone pair orbitals in  $C_{2v}$  molecules such as pyridine and  $C_s$  molecules such as 2-R-pyridine can be explained by differences in symmetry and, therefore, by mixing with other  $\sigma$ -orbitals.

Within a series of molecules with the same symmetry, however, the validity of this approach is further confirmed by the results of 2-aminopyridine. Four separate bands are observed in the region of 8 to 12 eV. These bands correspond to ionizations from the nitrogen lone pair of the pyridine ring, the two highest occupied  $\pi$ -orbitals of the pyridine ring and the amino lone pair. The lone pair of the amino nitrogen will interact with the  $\pi$ -system of the ring and is also called  $\pi$ . An assignment in the literature based on CNDO/2 calculations and a comparison with aniline and pyridine have led to the following orbital order:  $\pi_4, n, \pi_3, \pi_2$  [17].

From the correlation in the orbital energy diagram it appears that the  $\pi_3$ -orbital will have a much lower density on the nitrogen atoms compared to  $\pi_2$  and  $\pi_4$ . This is in complete agreement with our findings from He(I)/He(II) intensity changes. The intensity of the n-orbital slightly increases with respect to  $\pi_3$ ,

but decreases relative to  $\pi_2$  and  $\pi_4$ , as expected. In addition, the He(I) and He(II) spectra of a series of 4-substituted pyridines (methyl, tertiary butyl and cyano) were compared as well. Unfortunately all these spectra showed one very broad band with two broad maxima arising from the lone pair on nitrogen, the  $\pi(a_2)$ -orbital and the  $\pi(b_1)$ -orbital. The first two could not be distinguished and were both responsible for the first maximum. The second maximum became clearly stronger in the He(II) spectrum in all cases and could, therefore, evidently be attributed to the  $\pi(b_1)$ -orbital.

Our He(I)/He(II) results with the related pyrazine molecule confirm the assignments of Gleiter *et al.* [18] and v.d. Ham *et al.*, [19]. The  $\pi(b_{1g})$  band was strongly enhanced in He(II) compared to the  $\pi(b_{2g})$ .

We can conclude that the study of the changes in intensity of photoelectron bands on going from He(I) to He(II) leads to some simple rules such as:

a)  $\pi$ -orbitals with a high density on a nitrogen atom show a relatively strong increase in band intensity.

b) the lone pair orbital on nitrogen in molecules such as pyridine and pentafluoropyridine shows a relative decrease in intensity with respect to  $\pi$ -orbitals.

c) the lone pair orbital on nitrogen in  $\alpha$ -substituted pyridines shows a smaller relative decrease in intensity with respect to  $\pi$ -orbitals.

These rules gave us a useful assignment criterion in these series of closely related molecules.

### Acknowledgement

The authors thank Mr. H. van Dam for helpful discussions.

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