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The He I and He II ultraviolet photoelectron spectra of 2-fluoro-, 2-chloro-, 2-bromo-, and 2-iodopyridine have been recorded and interpreted in terms of a composite-molecule model. The sequence of the four lowest ionization energies for 2-fluoro- and 2-chloropyridine is:  $\pi_3 (1a_2) < n_N (11a_1) < \pi_2 (2b_1) < \sigma_{pyr} (7b_2)$ , whereas for 2-bromo- and 2-iodopyridine the assignment is:  $\pi_3 (1a_2) - \pi_X < n_N (11a_1) < \sigma_X < \pi_2 (2b_1)$ , where X represents a bromine and iodine lone-pair. Comparison of the He I and He II band intensities confirmed this assignment. However, ab initio calculations at the STO-3G\*\*//STO-3G\* and 6-31G\*\*//STO-3G\* levels did not agree with the sequence predicted by either the composite-molecule model, simple correlations and the He I/He II cross-section ratios. For the 2-fluoropyridine, a comparison using the HAM/3 model was found to be in agreement with this assignment.

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The electronic structure and ultraviolet photoelectron spectra (UPS) of pyridine and its substituted derivatives have been the subject of numerous experimental and theoretical investigations [1-10]. The difficulty in their UPS assignments centers on the interpretation of the lowest three ionization energies (IEs); one band is attributed to ionization from a non-bonding orbital localized on the nitrogen atom, while others arise from ionization of bonding and anti-bonding  $\pi$  orbitals delocalized over the ring and substituent(s).

Reliance on Koopmans' approximation (KA) using all electron Hartree-Fock (HF) MOs (denoted as the KA/HF model) fails to correctly interpret the UPS spectra of these compounds. For example, in the case of for pyridine and mono-substituted pyridines, Dunne *et al.* [10] have demonstrated that KA/HF model in conjunction with STO-3G or 6-31G\*\* basis sets do not ensure adequate cancellation of relaxation by correlation corrections. For pyridine the KA/HF/STO-3G and KA/HF/6-31G\*\* assignments give the order of the lowest three IEs as [10]:  ${}^2A_2(\pi_3) < {}^2B_1(\pi_2) < {}^2A_1(n_N)$ . Both experiment [1-2,6] and many-body Green's function calculations [5] yield the IE sequence as:  ${}^2A_1(n_N) \sim {}^2A_2(\pi_3) < {}^2B_1(\pi_2)$ . Dunne *et al.* [10] have demonstrated (using sophisticated configuration interaction calculations) that the underlying cause for the incorrect ordering of the KA/HF model in the case of mono-substituted pyridines was its inability to correctly assign the position of the  $n_N$  IEs, even though it adequately positions ionizations arising from the  $\pi$  orbitals.

Generally, IEs obtained *via* the HAM/3 method [6,11-13] have been shown to reliably predict the distribution of ionic states for a number of problematic molecules [11-13] containing first row atoms. (At present no parameterization is available for molecules containing more electron-dense atoms). Reasonable agreement with experiment is assured since this model takes into account mono-centric many-body effects and so directly incorporates both relaxation and correlation effects in the calculation

of IEs. Hence it is not surprising that for pyridine [10] and methoxypyridines [10] the HAM/3 method yields the first four IEs to within  $\sim 0.5$  eV of experiment and so is the method of choice as an assignment tool for molecules containing first row atoms (such as for 2-fluoropyridine).

As an extension of our earlier work on the electronic structure of the monosubstituted pyridines [10] and the chalcogenobispyridines [14-18], we have investigated the He I and He II UPS spectra of the 2-halopyridines. Only the first few IEs have been previously recorded for 2-fluoro-[8], 2-chloro-[9] and 2-bromopyridine [3] in which the assignments were mostly based on their He I spectra. However, in this study we shall present both the He I and He II spectra for all the members of the 2-halopyridine family (including 2-iodopyridine for which the UPS spectrum has not yet been characterized). Furthermore, we shall table and assign all twelve vertical IEs below 20 eV using composite-molecule model, comparisons between He I and He II band intensities and ab initio calculations.

#### Calculations.

Ab initio electronic calculations were performed using the GAUSSIAN 88 suite of programs [19] and the internal STO-3G and 6-31G\*\* basis sets. The valence double zeta 6-31G\*\* basis set is chemically more reliable, yielding values close to the HF limit for CC, CN, NN and CO bonds [20-21]. On the other hand, the STO-3G basis set is more tractable and due to fortuitous cancellations, the mean absolute deviation from experiment for SCF bondlengths has been reported to be 0.03 Å for a large number of molecules containing C, H, N, O and F [22]. This is of sufficient geometrical accuracy for use in UPS investigations. Hence both the 6-31G\*\* basis set at the STO-3G\* optimized geometry (denoted 6-31G\*\*//STO-3G\*) and the STO-3G\*\*//STO-3G\* model were employed to calculate KA IEs in order to assist with the assignment with 2-fluoro- and 2-chloropyridine. In the case of

2-fluoropyridine, the HAM/3 model was also employed.

There are no 6-31G\*\* basis sets available for third and fourth row atoms. In order to supplement the STO-3G\*\*//STO-3G\* model, further calculations were conducted for 2-bromopyridine and 2-iodopyridine using 6-31G\*\* basis set for hydrogen, carbon and nitrogen atoms, but using the minimum basis set contractions schemes of Csizmadia *et al.* [23] for the bromine and iodine atoms. The contracted basis set for bromine and iodine atoms are the [11s8p3d/4s3p1d] and [13s10p6d/5s4p2d] constructions respectively. For convenience we shall denote these calculations as the 6-31G\*\*//STO-3G\* model, even though this designation is not strictly appropriate for the bromine and iodine atoms.

There is no crystallographic data for the 2-halopyridines. Hence optimizations of the critical geometrical parameters for these compounds may be of interest. All

Table 1

Comparison of STO-3G\*\*//STO-3G\* Optimized Parameters of the 2-Halopyridines with Experimental Values for Halobenzenes

Substituent	2-Halopyridines		Halobenzenes [a]	
	R <sub>C-X</sub> (Å)	A <sub>N-C-X</sub> (Deg.)	R <sub>C-X</sub> (Å)	A <sub>N-C-X</sub> (Deg.)
Fluoro-	1.35	115.7	1.34	120
Chloro-	1.75	116.1	1.71	120
Bromo-	1.74	116.1	1.86	120
Iodo-	1.91	116.1	2.08	120

[a] See reference [26]. All valence angles are assumed to be 120°.

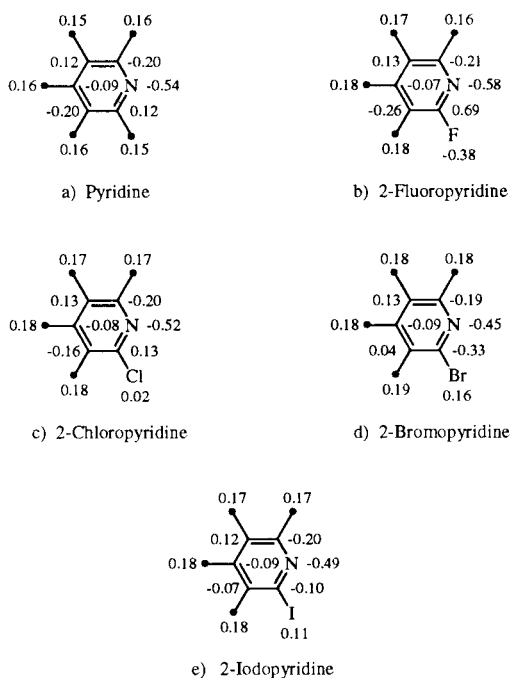


Figure 1: 6-31G\*\*//STO-3G\* electronic distribution of: (a) pyridine; (b) 2-fluoropyridine; (c) 2-chloropyridine; (d) 2-bromopyridine; (e) 2-iodopyridine.

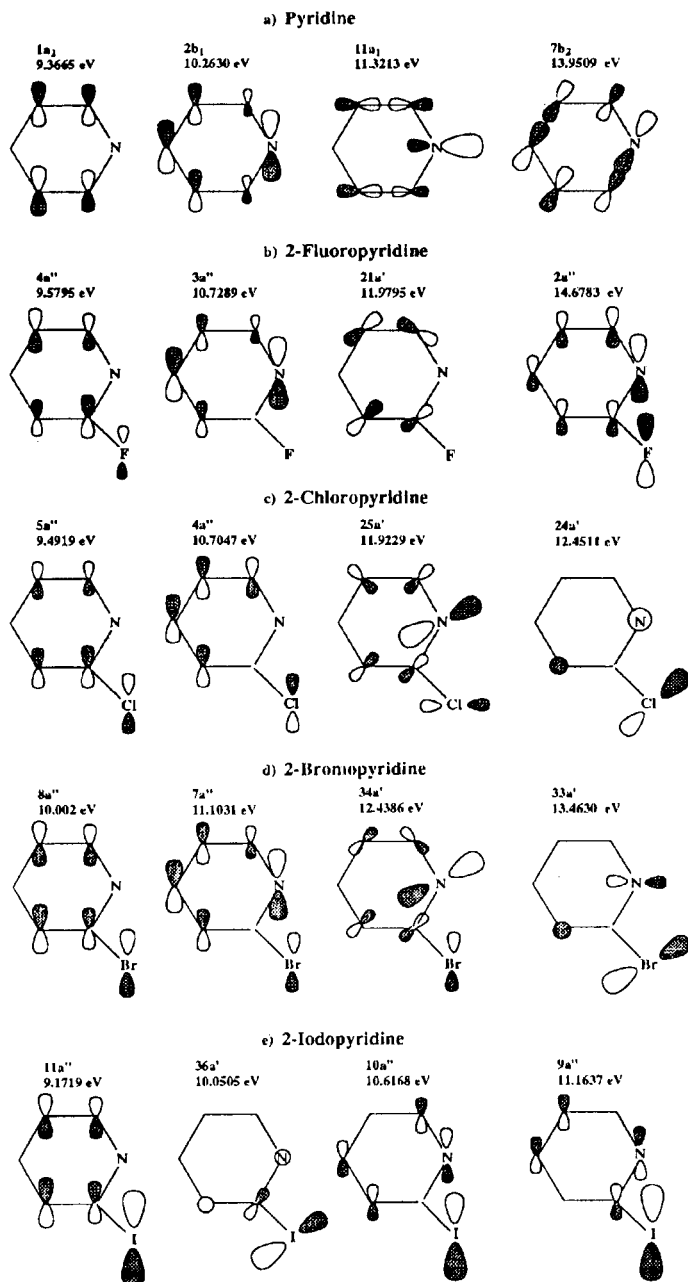


Figure 2: Highest four occupied MOs calculated using the 6-31G\*\*//STO-3G\* model for: (a) pyridine; (b) 2-fluoropyridine; (c) 2-chloropyridine; (d) 2-bromopyridine; (e) 2-iodopyridine.

optimizations were carried out using the STO-3G\* basis set and the Fletcher-Powell algorithm [24]. The geometry of the pyridine ring was fixed and is essentially that reported by Del Bene [25]. Each of the four 2-halopyridines is planar and of C<sub>s</sub> symmetry, differing only by the carbon-halogen bond length, R<sub>C-X</sub>, and the angle of this bond to the pyridine ring, A<sub>N-C-X</sub>. Table 1 compares the optimized values of the critical parameter, R<sub>C-X</sub>, with those obtained from crystallographic data for the halobenzenes [26].

Table 2  
Comparison of Experimental and Theoretical IEs (in eV) for 2-Halopyridines

Expt	Assignment [a]	STO-3G**/STO-3G*	6-31G**/STO-3G*
(a) 2-Fluoropyridine [b]			
9.89 (9.85)	$\pi_3(1a_2)$	7.93 (10.02)	9.58
10.42 (10.45)	$n_N(11a_1)$	12.55 (10.25)	14.85
10.87 (10.85)	$\pi_2(2b_1)$	9.00 (10.92)	10.73
13.37	$\sigma_{pyr}(7b_2)$	9.55 (13.41)	11.98
13.37	$\pi_1(1b_1)$	12.72 (12.79)	14.68
13.96	$\sigma_{pyr}(10a_1)$	13.27 (13.89)	15.84
14.56	$\sigma_{pyr}(6b_2)$	14.57 (14.55)	16.90
15.41	$\sigma_{pyr}(9a_1)$	15.31 (15.53)	17.18
16.32	$n_F$	15.55 (16.16)	18.83
16.83	$\sigma_{pyr}(5b_2)$	17.15 (16.23)	20.57
16.83	$\sigma_F$	16.74 (17.85)	18.75
17.79	$\sigma_{pyr}(8a_1)$	18.42 (16.40)	19.49
(b) 2-Chloropyridine [c]			
9.63 (9.68)	$\pi_3(1a_2)$	8.36	9.49
10.12 (10.18)	$n_N(11a_1)$	9.92	11.92
10.72 (10.77)	$\pi_2(2b_1)$	9.30	10.70
11.50 (11.53)	$\sigma_{pyr}(10a_1) - \sigma_{Cl}$	10.84	12.45
12.06 (12.08)	$\pi_1(1b_1) - \pi_{Cl}$	11.57	12.94
13.12	$\sigma_{pyr}(7b_2)$	14.55	15.97
13.92	$\pi_1(1b_1) + \pi_{Cl}$	14.54	15.55
13.92	$\sigma_{pyr}(10a_1) + \sigma_{Cl}$	12.79	14.44
14.62	$\sigma_{pyr}(6b_2)$	15.11	16.37
15.67	$\sigma_{pyr}(9a_1)$	16.66	17.85
16.19	$\sigma_{pyr}(5b_2)$	17.06	18.57
17.02	$\sigma_{pyr}(8a_1)$	18.50	19.55
(c) 2-Bromopyridine [d]			
9.17 (9.2)	$\pi_3(1a_2) - \pi_{Br}$	7.33	10.00
9.69	$n_N(11a_1)$	8.92	12.44
10.54 (10.48)	$\sigma_{Br}$	9.55	13.46
10.59	$\pi_2(2b_1)$	8.92	11.10
11.29	$\pi_3(1a_2) + \pi_{Br}$	10.54	13.85
12.59	$\pi_1(1b_1)$	14.18	16.43
13.71	$\sigma_{pyr}(10a_1)$	12.20	15.01
13.91	$\sigma_{pyr}(7b_2)$	14.05	16.39
14.53	$\sigma_{pyr}(6b_2)$	14.68	16.74
15.63	$\sigma_{pyr}(9a_1)$	16.26	18.13
16.24	$\sigma_{pyr}(5b_2)$	16.72	19.18
17.26	$\sigma_{pyr}(8a_1)$	17.99	19.67
(d) 2-Iodopyridine			
9.09	$\pi_3(1a_2) - \pi_I$	7.13	9.17
9.67	$n_N(11a_1)$	9.23	11.52
10.05	$\sigma_I$	7.59	10.05
10.59	$\pi_2(2b_1)$	8.99	10.62
10.97	$\pi_3(1a_2) + \pi_I$	9.44	11.16
12.29	$\pi_1(1b_1)$	13.97	15.29
13.41	$\sigma_{pyr}(7b_2)$	11.01	13.19
13.89	$\sigma_{pyr}(10a_1)$	13.76	15.51
14.54	$\sigma_{pyr}(6b_2)$	14.70	16.24
15.56	$\sigma_{pyr}(9a_1)$	16.13	17.67
16.07	$\sigma_{pyr}(5b_2)$	16.64	18.52
16.94	$\sigma_{pyr}(8a_1)$	17.54	19.38

[a] Preferred assignment. [b] Experimental IEs in brackets obtained from reference [8]. HAM/3//STO-3G\* IEs are in brackets under the STO-3G\*\*/STO-3G\* heading. [c] Experimental IEs in brackets obtained from reference [9]. [d] Experimental IEs in brackets obtained from reference [3].

Figure 1 gives the electronic distribution resulting from the 6-31G\*\*//STO-3G\* calculations. The calculations indicate that only the fluorine substituent is sufficiently electronegative in order to be an effective electron withdrawer, whereas for chloro-, bromo- and iodopyridines the resonance interaction of the np AOs on the halogen substituent with the pyridyl  $\pi$  fragment orbitals (FOs) results in the halogen substituent donating electron density into the ring.

Figure 2 gives the four lowest occupied MOs from the 6-31G\*\*//STO-3G\* calculations on pyridine and the 2-halopyridines. For 2-fluoro-, 2-chloro-, 2-bromo- and 2-iodopyridine this model predicts the  $n_N$  IE to be the 5th, 3rd, 3rd and 5th ionization energy respectively. Table 2 gives the calculated KA IEs accessible to He I radiation using HAM/3//STO-3G\* (2-fluoropyridine only), STO-3G\*//STO-3G\* and 6-31G\*\*//STO-3G\* models. In the case of the STO-3G\*//STO-3G\* and 6-31G\*\*//STO-3G\* models the sequence of the KA IEs for 2-chloro- and 2-bromopyridine do not differ, whereas for 2-fluoro- and 2-iodopyridine significant differences are evident. For 2-fluoropyridine neither model is in agreement with the HAM/3//STO-3G\* calculation.

## EXPERIMENTAL

2-Fluoro-, 2-chloro- and 2-bromopyridine was obtained from Aldrich, but was further purified. The 2-iodopyridine is extremely light sensitive and so decomposes readily. It had to be prepared prior to UPS analysis. The method used to synthesize 2-iodopyridine was the method of Baker, Curtis and Edwards [27]. The resultant product was characterized using  $^1\text{H}$  and  $^{13}\text{C}$  nmr and the purity verified from chemical shifts given in the literature.

Due to the fact that all the 2-halopyridines are relatively high vapor pressure liquids, the gas inlet system of Perkin-Elmer PS 16/18 spectrometer was used. The spectra of the 2-halopyridines were recorded with oil temperatures in the range 30-40°. The operating resolution was between 25-35 meV. Each spectrum was accumulated over a ~20 minute period and was repeated several times in order to ensure reproducibility. Furthermore, the spectra were calibrated using butadiene/argon gas mixtures.

The PS 16/18 spectrometer has been modified to accommodate a Helios helium lamp and so can output both He I (21.2 eV) and He II (40.8 eV) radiation. The He I and He II spectra of the 2-halopyridines are given in Figures 3 and 4 respectively. Under He I and He II conditions the maximum band intensity is of the order of 1000 and 100 counts per second respectively.

The s-p separation rule [28] was used to predict the number of p-based bands below 18 eV. The number of these bands is given by,

$$N_T = N_C + 0.5N_H + 1.5N_N + 2.5N_X \quad (1)$$

where  $N_C$ ,  $N_H$ ,  $N_N$  and  $N_X$  are the number of carbon, hydrogen, nitrogen and halogen atoms in the molecule respectively. For pyridine, equation (1) gives 9 p-based bands and, allowing for a

cross-over of an s- and p-based band occurring in the 15-18 eV region [1-2], a total of 10 bands are predicted for below 18 eV. Hence, in the case of the halopyridines, equation (1) predicts 11 p-based bands and with the corresponding crossover a total of 12 bands are expected below 18 eV. Table 2 gives the twelve experimental vertical ionizations for the 2-halopyridines and compares them with other experimentally measured values and theoretical KA IEs. The agreement between the measured IEs (where such comparisons can be made [1-4,6-9]) is within spectral resolution.

All spectra were digitized for use in the density-of-states analysis [14]. The density-of-states analysis assumes that band intensity is a measure of orbital degeneracy, so that where bands are strongly overlapped the total band area in each separable region of the spectrum is related to the number of occupied orbitals. Table 3 gives the experimental density-of-states analysis.

The photoionization cross-section varies as a function of photon energy. An effective measure of the variation on band intensity on going from He I to He II radiation is given by [8],

$$\% \text{ Change} = [( \text{He II Band Intensity} / \text{He I Band Intensity} ) - 1] * 100 \quad (2)$$

A negative (positive) percentage change indicates a reduction (enhancement) on going from He I to He II radiation. Table 4 gives the relative He I and He II band intensities and percentage change for the 2-halopyridines.

## Discussion.

Del Bene [29] has calculated the 2-fluoropyridine geometry using the STO-3G//STO-3G model. Her optimized critical parameters,  $R_{C-F}$  and  $A_{N-C-F}$ , are 1.35 Å and 116° respectively, in excellent agreement with the optimized values given in Table 1 (as would be expected because of the similarity of the models). Although no optimized values are available for the other members of the 2-halopyridine family, comparison with the experimental geometries of the halobenzenes illustrate that the maximum difference in the bondlength is only 0.17 Å for the iodo compound. Furthermore as would be anticipated, the bondlength  $R_{C-X}$  increases with increasing ionic radii of the halogen substituent.

Figure 1 shows that the fluorine substituent is sufficiently electronegative in order for it to be an effective electron withdrawer (which is also consistent with the calculations of Del Bene [29]). Therefore the fluorine dominated MOs should be at higher IE than those localized on the pyridyl  $\pi$  fragment. However, for the more electronegative members of the family the resonance interaction of the np AOs on the halogen substituent with the pyridyl  $\pi$  FOs results in the halogen substituent donating electron density into the ring. This is consistent with the Pariser-Parr-Pople (PPP) calculations of Martins [30] and with the interpretation of UPS spectra of the halobenzenes [2].

Figure 2 shows that the calculated MOs may be interpreted in terms of a composite-molecule model. That is, the molecule can be defined in terms of two subunits (*i.e.* the halogen substituent and pyridyl moiety) enabling a

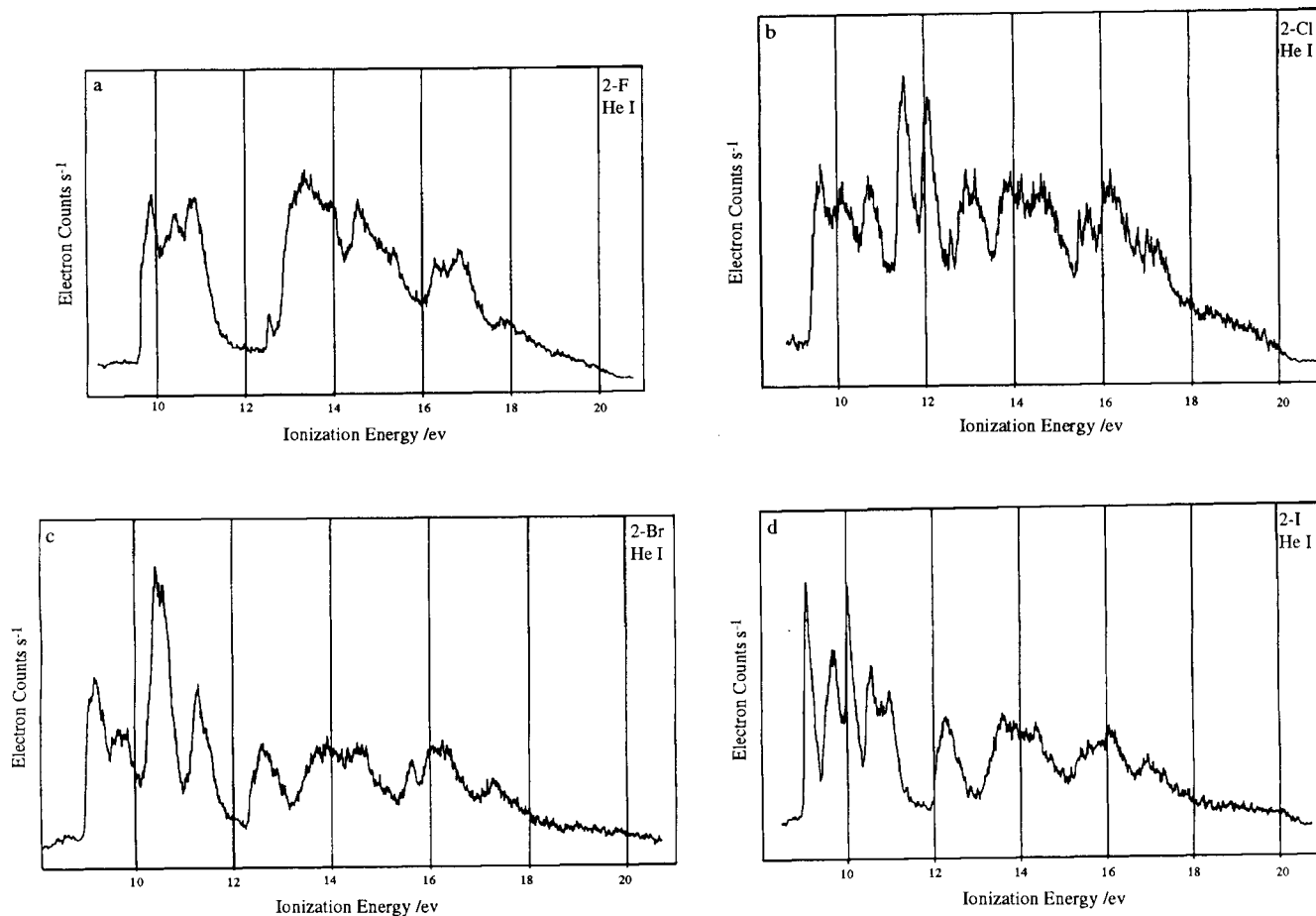


Figure 3: The differential He I spectrum of: (a) 2-fluoropyridine; (b) 2-chloropyridine; (c) 2-bromopyridine; (d) 2-iodopyridine.

composite MO to be obtained by using a linear combination of FOs delocalized over each fragment. As a consequence the composite-molecule model can be constructed from the nine p-based FOs of the pyridine molecule [6] and three p-based FOs of the halogen substituent. Table 2 gives the composite-molecule model identification of each KA IE of the 2-halopyridines.

From Table 2 it is evident that for both the STO-3G\*\*//STO-3G\* and 6-31G\*\*//STO-3G\* models, the order of the lowest KA IEs for the 2-halopyridines is contrary to the assignment of pyridine [6] and to the methoxypyridines [10] (which has at least one  $\pi$  band at higher IE than the  $n_N$  band). In the case of the methoxypyridines, Dunne *et al.* [10] found that the HAM/3 method correctly assigned all the isomers, even in cases where more sophisticated ab initio models erred. As a consequence, total reliance on KA IEs for both the STO-3G\*\*//STO-3G\* and 6-31G\*\*//STO-3G\* models is not appropriate in pyridine [10] and moreover, in mono-substituted pyridines [10].

Table 3 gives a comparison of the experimental He I band intensities with the calculated IE distributions using the STO-3G\*\*//STO-3G\* and 6-31G\*\*//STO-3G\* models.

For 2-fluoropyridine the HAM/3//STO-3G\* calculation is also included. While there are deficiencies in adopting the sequence of KA IEs in isolation, it would be anticipated that the distribution of the IEs would be more adequately predicted. For 2-fluoro-, 2-chloro-, 2-bromo- and 2-iodopyridine the experimental distribution (taking into account the analyzer discrimination against slow moving electrons) is given as (3:3:2:4), (2:3:4:3), (2:3:4:3) and (5:1:3:3) in the respective regions. For the 2-fluoropyridine the HAM/3//STO-3G\* calculation gives the "best" IE distribution. This is consistent with the methoxypyridines [10] where the HAM/3//STO-3G\* calculation yields a better IE distribution than a configuration interaction model. For the more electron-dense 2-halopyridines, the 6-31G\*\*//STO-3G\* model is marginally superior to the STO-3G\*\*//STO-3G\* IE distributions.

For 2-fluoropyridine, HAM/3 gives the IE sequence  $\pi_3$  ( $1a_2$ ) <  $n_N$  ( $11a_1$ ) <  $\pi_2$  ( $2b_1$ ), which is consistent with the UPS assignment of other mono-substituted pyridines [10]. The introduction of a fluorine substituent results in different IE shifts for the  $\sigma$  and  $\pi$  bands of the pyridyl moiety. Due to the strong inductive effect of fluorine, the  $\sigma$  bands are shifted more dramatically to lower IE than the  $\pi$  bands

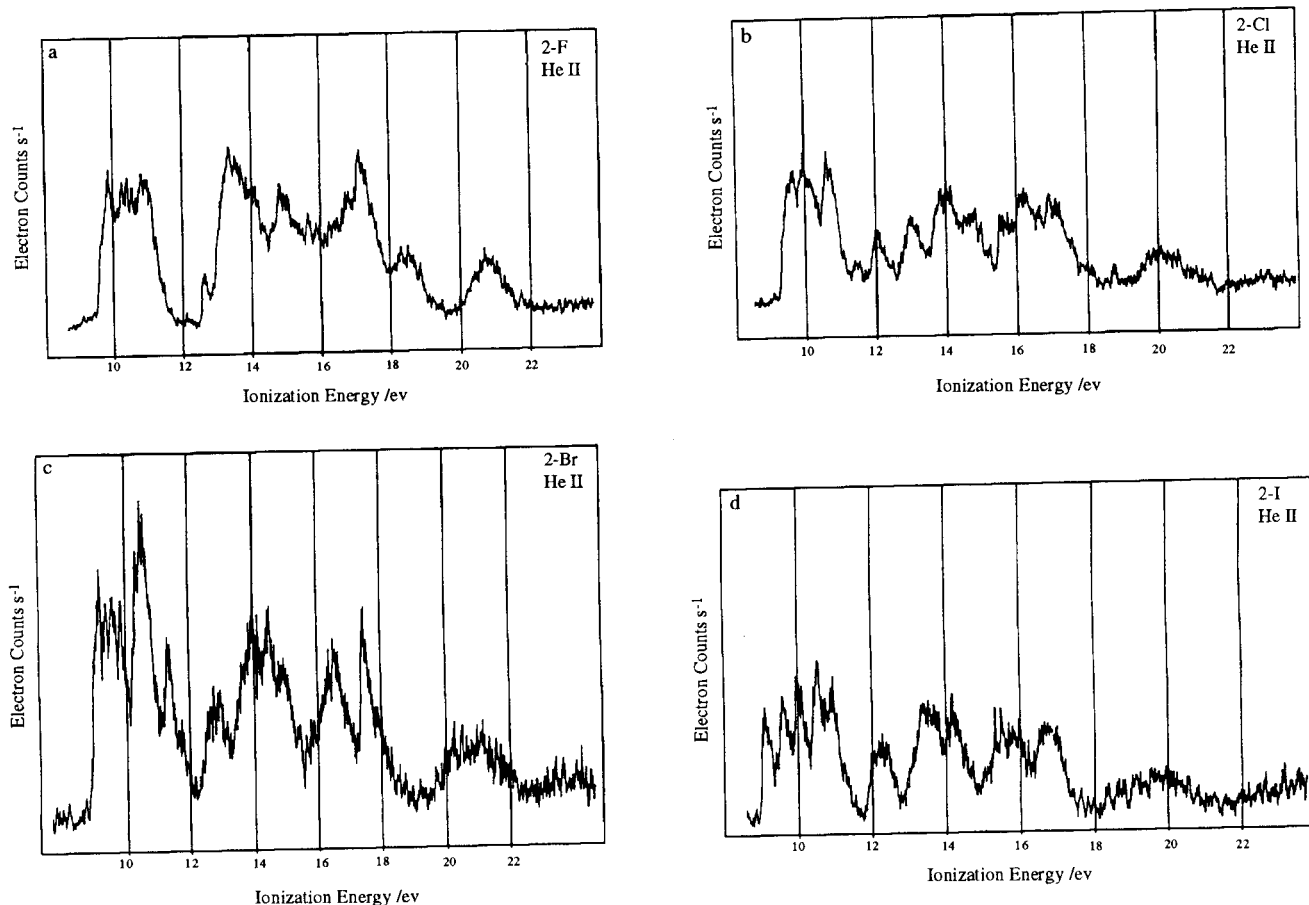


Figure 4: The differential He II spectrum of: (a) 2-fluoropyridine; (b) 2-chloropyridine; (c) 2-bromopyridine; (d) 2-iodopyridine.

(so called "perfluoro" effect [8]). Assuming that the first two bands are in accordance with the HAM/3//STO-3G\* calculation then the UPS spectrum of 2-fluoropyridine suggests that the shift from pyridine IEs is of the order  $\sim 0.8$  eV and 0.3 eV for the  $\sigma$  and  $\pi$  bands respectively (which is in keeping with the "perfluoro" effect in the UPS of aromatic compounds [2]).

The fluorine lone-pair is typically located  $\sim 16$  eV in a number of molecules [2]. For the 2-fluoropyridine Table 4 shows there is only a small reduction on going from He I to He II radiation in the region 9-16 eV and so suggesting that the mixture of  $n_F$  with pyridyl  $\pi$  FOs is small. The band at 16.32 eV reduces intensity dramatically, although on a whole the region between 16-18 eV shows an intensity enhancement (due to the presence of an additional three pyridyl based bands in this region). The percentage change on going from He I to He II radiation is in keeping with the fluorine lone-pair being assigned at 16.32 eV.

Simple correlations with the accepted assignment of pyridine [6] and the IEs of 2-fluoropyridine, the "perfluoro-" effect, HAM/3//STO-3G\* calculations, He I/He II band intensity comparisons give the preferred compos-

ite-molecule model assignment in Table 2. The assignment of the three lowest IEs is also consistent with previous He I assignments of 2-fluoropyridines [8].

In the case of the 2-chloropyridine the He I/He II study indicates an intensity enhancement occurs in the 9.3-11.2 eV region on going from He I to He II radiation (which is consistent with ionization arising from MOs composed mainly of C, N and H character). The preferred assignment in this region is:  $\pi_3 (1a_2) < n_N (11a_1) < \pi_2 (2b_1)$ , which is consistent with the 2-fluoropyridine assignment. A dramatic reduction in intensity would indicate the presence of chlorine character in the MO. Such a reduction occurs in the 11.2-13.4 eV region, a region in which the chlorine lone-pairs are typically assigned for a number of compounds [2]. The preferred composite-molecule assignment of 2-chloropyridine is given in Table 2. This assignment is also consistent with the order of the first four IEs given by Modelli and Distefano [9], which was constructed from their He I study of all three isomers of chloropyridines.

The bromine lone-pair orbitals are typically located at 10.5 eV for a number of compounds [2] and so can significantly interact with the  $\pi_3$  of the pyridyl moiety. The in-

Table 3

Comparison of Experimental Band Intensities and Calculated IE Distributions for 2-Halopyridines

IE Range (eV)	Band Intensity	Calculated IE Distribution	
	Expt [a]	STO-3G*	6-31G** [b]
(a) 2-Fluoropyridine			
9.44-12.00	3.53	1	3 (3)
12.00-14.25	3.53	3	- (3)
14.25-16.05	2.94	3	3 (2)
16.05-18.60	2.01	3	2 (4)
(b) 2-Chloropyridine			
9.27-11.19	2.63	3	2
11.19-12.61	2.48	1	2
12.61-15.37	3.99	4	2
15.43-18.00	2.90	2	4
(c) 2-Bromopyridine			
8.59-10.12	2.04	3	1
10.12-12.00	3.55	1	1
12.00-15.43	3.57	4	4
15.43-19.08	2.85	3	4
(d) 2-Iodopyridine			
8.75-11.76	5.31	4	5
11.76-12.99	1.19	-	-
12.99-14.85	2.49	3	1
14.85-18.00	3.00	3	4

[a] Based on the He I band intensities, normalized to 12 bands (see equation (1)). [b] Values in brackets are the HAM/3//STO-3G\* IEs.

plane bromine lone-pair is of  $\sigma$  symmetry and so is relatively unshifted from its molecular value at 10.54 eV. The He I/He II study confirms this assignment, since in the 8.5-10.1 eV region there is a small enhancement of intensity (*i.e.* 11% as compared to 63% for 2-chloropyridine) on going from He I to He II radiation. This is consistent with ionization from MOs composed mainly of C, N, H character, but with an Br AO presence. In the 10.1-11 eV region reduction occurs on going from He I to He II radiation (which indicates the presence of bromine character in the MO). The latter region is where the bromine bands are assigned. With this in mind and using simple correlation with the lowest energy IEs 2-fluoro- and 2-chloropyridine, the sequence for 2-bromopyridine in this region is:  $\pi_3 (1b_1) - \pi_{Br} < n_N (11a_1) < \sigma_{Br} < \pi_2 (2b_1)$ . The preferred assignment for the 2-bromopyridine in terms of a composite-molecule model is given in Table 2.

In the case of 2-iodopyridine the iodine lone-pairs are typically located  $\sim 9.9$  eV [2] and so significant resonance interaction can occur with the lowest energy  $\pi$  bands of the pyridyl moiety. The in-plane iodine lone-pair is of  $\sigma$  symmetry and so remains relatively unshifted from its

Table 4

Relative He I and He II Band Intensities and Percentage Change for 2-Halopyridines

IE Range (eV)	Experimental Band Intensities		% Change
	He I	He II	
(a) 2-Fluoropyridine			
9.44-12.00	3.53	3.19	-9.6
12.00-14.25	3.53	2.94	-16.7
14.25-16.05	2.94	2.51	-14.6
16.05-18.60	2.01	3.36	67.2
(b) 2-Chloropyridine			
9.27-9.81	0.68	1.11	63.2
9.81-10.48	1.03	1.42	37.9
10.48-11.19	0.95	1.21	27.4
11.19-12.61	2.49	1.15	-53.8
12.61-13.43	1.20	0.96	-20.0
13.43-15.37	2.77	2.79	0.7
15.37-18.00	2.88	3.36	16.7
(c) 2-Bromopyridine			
8.59-10.12	2.04	2.26	11.3
10.12-11.01	2.31	1.90	-17.7
11.01-12.00	1.27	1.00	-21.3
12.00-15.43	3.55	3.69	3.9
15.43-19.08	2.84	3.16	21.3
(d) 2-Iodopyridine			
8.75-9.34	1.04	0.65	-51.9
9.34-9.86	1.17	0.90	-23.1
9.86-10.34	1.27	0.96	-24.4
10.34-11.76	1.96	2.21	12.8
11.76-12.99	1.18	1.22	3.4
12.99-14.85	2.44	3.12	27.9
14.85-18.00	2.94	2.95	0.3

[a] Normalized to 12 bands (see equation (1)). [b] See equation (2).

molecular value at 10.05 eV. The He I/He II study confirms its location, since in the 8.8-10.3 eV region there is a reduction of intensity on going from He I to He II radiation, which is consistent with ionization from MOs composed mainly of iodine character. Using simple correlation with the lowest energy IEs of 2-bromopyridine, the preferred sequence for 2-iodopyridine is:  $\pi_3 (1a_2) - \pi_1 < n_N (11a_1) < \sigma_1 < \pi_2 (2b_1)$ . The composite-molecule model assignment is given in Table 2.

### Conclusion.

The UPS spectra of 2-halopyridines can be interpreted using a composite-molecule model which is based on linear combination of FOs localized on the pyridyl moiety and on the halogen substituent. The sequence for the four lowest ionization energies of the 2-fluoro- and 2-chloropyridine is:  $\pi_3 (1a_2) < n_N (11a_1) < \pi_2 (2b_1) < \sigma_{pyr} (7b_2)$ , whereas for 2-bromo- and 2-iodopyridine the assignment

is:  $\pi_3(1a_2) - \pi_X < n_N(11a_1) < \sigma_X < \pi_2(2b_1)$ . Comparison of the He I/He II band intensities ratios, simple correlations with pyridine [6] and other mono-substituted pyridines [9-10] and (in the case of 2-fluoropyridine) HAM/3//STO-3G\* calculations confirmed this assignment. However, ab initio calculations at the STO-3G\*//STO-3G\* and 6-31G\*\*//STO-3G\* levels yields an incorrect assignment, due to the inability of these models to correctly assign the position of the  $n_N$  IE.

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