HeI and HeII Spectra of 3-Halopyridines

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The ultraviolet photoelectron spectra (UPS) of 3-fluoro-, 3- chloro-, 3-bromo- and 3- iodopyridine were recorded and interpreted using a composite-molecule model. The sequence of the four lowest ionization energies for 3-fluoro- and 3-chloropyridine is: π_3 ($1a_2$) < n_N ($11a_1$) < π_2 ($2b_1$) < σ_{pyr} ($7b_2$), whereas for 3-bromo- and 3-iodopyridine the assignment is: π_3 ($1a_2$) - π_x < n_N ($11a_1$) < σ_x< π_2 ($2b_1$) (where X represents a bromine or iodine lone-pair). Comparison of the HeI and HeII band intensities and correlations with the UPS assignment of the 2-halopyridines confirm this sequence. However, ab initio calculations using the STO-3G*//STO-3G* and 6-31G**//STO-3G* models do not agree with either the composite-molecule model, simple UPS correlations and HeI/HeII cross-section ratios. For 3-fluoropyridine, the HAM/3 model was in agreement with the proposed assignment.

Introduction.

The ultraviolet photoelectron spectra (UPS) of pyridine and its substituted derivatives continues to be of interest to both theoreticians and experimentalists alike [1-10]. The synergy between theory and experiment finally resolved the interpretation of the lowest three ionization energies (IEs) of pyridine; one band is due to ionization from a non-bonding orbital localized on the nitrogen atom (labelled n_N), while the other two are due to ionizations arising from bonding and anti-bonding combinations of π orbitals delocalized over the ring moiety. The accepted IE sequence for pyridine is: $^2A_1(n_N)$ ~ $^2A_2(\pi_3)$ < $^2B_1(\pi_2)$.

Koopmans' approximation (KA) based on the all electron Hartree-Fock (HF) MOs (denoted as KA/HF models) fails to correctly assign the UPS spectra of pyridine compounds. For pyridine, the KA/HF/STO-3G and KA/HF/6-3 1G** model yield the IE sequence: $^2A_2(\pi_3)$ < $^2B_1(\pi_2)$ < $^2A_1(n_N)$, which is both contrary to experiment [1-2, 6] and many-body Green's function calculations [5]. Dunne *et al.* [10] have shown that this failure rests on the inability of KA/HF models to correctly assign the position of the n_N IEs, even though ionizations arising from the π orbitals are adequately positioned.

For UPS interpretation of pyridine compounds focus has centred on semi-empirical MO methods which incorporate correlation effects. Generally, the IEs obtained from the HAM/3 method [6,11-13] were shown to reliably predict the electronic structure of a number of problematic molecules [11-13] containing first row atoms. Agreement between the HAM/3 and experimental IEs centres on HAM/3 model incorporating monocentric many-body effects. The method implicitly includes both relaxation and correlation effects in the calculation of IEs. It is therefore not surprising that for pyridine and methoxypyridines [10] the HAM/3 method yields the first four IEs to within ~0.5 eV of experiment. The HAM/3 model is the method of choice as an assignment tool for molecules containing first

row atoms (such as for 3-fluoropyridine). However, at present parameterization is not coded for molecules containing chlorine, bromine and iodine atoms and so for halopyridines this method is only available for fluoropyridine.

As an extension of our earlier work on the electronic structure of pyridine and its the mono-substituted compounds [10,14-15], we have investigated the HeI and HeII spectra of the 3-halopyridines. Only the first few IEs have been reported for 3-chloro-[3,9] (the assignments being primarily based on their He I spectra). In this investigation we shall present both the HeI and HeII spectra for all the members of the 3-halopyridine family. Furthermore, we shall table and assign all twelve vertical IEs below 20 eV (using a composite-molecule model) and give comparisons
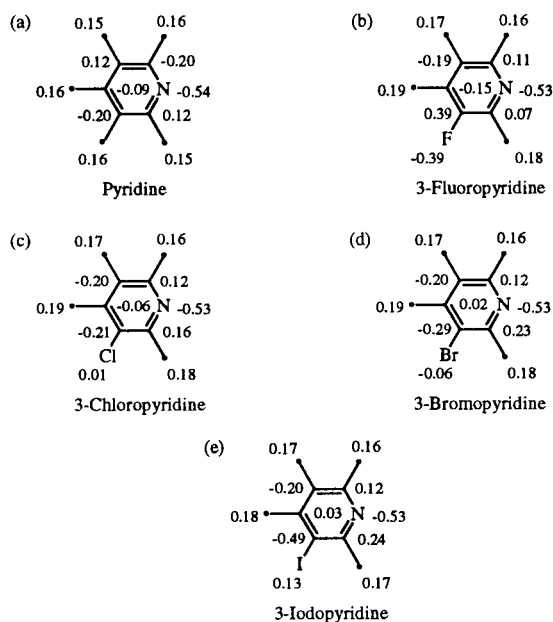

Figure 1. The 6-31G**//STO-3G* electonic distribution of : (a) pyridine; (b) 3-fluoropyridine; (c) 3-chloropyridine; (d) 3-bromopyridine; (e) 3-iodopyridine.

a) Pyridine

1a₂ — 1a$_2$

| 1a$_2$ 9.3665 eV | 2b$_1$ 10.2630 eV | 11a$_1$ 11.3213 eV | 7b$_2$ 13.9509 eV |

b) 3-Fluoropyridine

| 4a" 9.5134 eV | 3a" 10.6418 eV | 21a' 11.7713 eV | 2a" 14.7379 eV |

c) 3-Cloropyridine

| 5a" 9.4519 eV | 4a" 10.6116 eV | 25a' 11.6995 eV | 24a' 12.8149 eV |

d) 3-Bromopyridine

| 8a" 9.3161 eV | 7a" 10.5888 eV | 34a' 11.3765 eV | 33a' 12.0081 eV |

e) 3-Iodopyridine

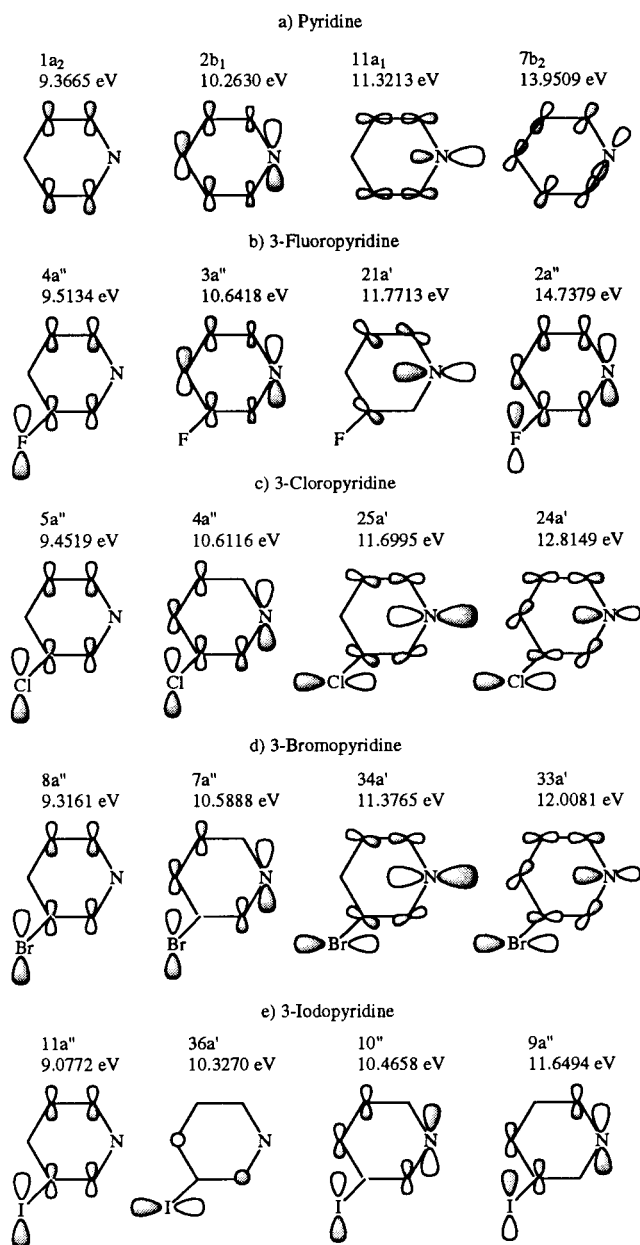| 11a" 9.0772 eV | 36a' 10.3270 eV | 10" 10.4658 eV | 9a" 11.6494 eV |

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

between HeI and HeII band intensities, correlations with the UPS assignment of the 2-halopyridines [3,9,15] as well as comparisons with ab initio calculations.

Calculations.

All the electronic calculations were performed using the GAUSSIAN 92 suite of programmes [16] with either the internal STO-3G* or 6-31G** basis sets. The STO-3G* basis set is tractable and due to fortuitous cancellations at the HF level yields reliable geometries, especially for molecules containing first row atoms. For example, the mean deviation between experimental and calculated bond lengths for a large number of molecules containing C, H, N, O and F atoms is 0.03 Å [17]. This is of sufficient geometrical accuracy for use in UPS calculations. On the other hand, the valence double zeta 6-31G** basis set (including p and d polarization functions) is chemically more reliable [18-19]. The 6-31G** basis set was shown to be reliable in predicting the π IEs of the pyridyl moieties [10]. Hence both the 6-31G** basis set at the STO-3G* optimized geometry (denoted 6-31G**//STO-3G*) and the STO-3G*//STO-3G* models were used to calculate KA IEs of 3-fluoro and 3-chloropyridine. In the case of 3-fluoropyridine, HAM/3 model [11-13] was also employed, since it was shown to be reliable in predicting the n$_N$ IEs [10, 14-15].

There are no 6-31G** basis sets available for third and fourth row atoms. Nevertheless, further calculations were conducted for 3-bromo and 3-iodopyridine using 6-31G** basis set for hydrogen, carbon and nitrogen atoms, but using the minimum basis set contractions [11s8p3d/-4s3pld] and [13s10p6d/5s4p2d] for the bromine and iodine atoms respectively [20]. For convenience in labeling, we shall denote these calculations as 6-31G**//STO-3G*, even though this designation is not appropriate for the bromine and iodine atoms.

There is no crystallographic data for the 3-halopyridines. Therefore optimizations of the critical geometrical parameters for the 3-halopyridines will be of general interest. All optimizations were performed with the STO-3G* basis set using the Fletcher-Powell algorithm [21]. The geometry of the pyridine ring was fixed to that of the optimized structure of Del Bene [22]. Each of the halopyridines is of

Table 1

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

| Substituent | 3-Halopyridines | | 2-Halopyridines (Halobenzenes) [a] | |
	R_{C-X} (/Å)	A_{N-C-X} (/Deg.)	R_{C-X} (/Å)	A_{N-C-X} (/Deg.)
Fluoro-	1.35	120.0	1.35 (1.34)	115.7 (120)
Chloro-	1.74	119.8	1.75 (1.71)	116.1 (120)
Bromo-	1.84	120.1	1.74 (1.86)	116.1 (120)
Iodo-	2.07	120.2	1.91 (2.08)	116.1 (120)

[a] For the 2-halopyridine calculated values see reference [15]. The values in brackets are the experimental values for the halobenzenes reported in reference [24] for which all valence angles were assumed to be 120°.

Table 2

Comparison of Experimental and Theoretical IEs (in eV) for 3-Halopyridines

Expt	Assign [a]	STO-3G*//STO-3G*	6-31G**//STO-3G*
(a) 3-Fluoropyridine [b]			
9.50	π_3 (1a$_2$)	7.88 (9.95)	9.51
10.50	n$_N$ (11a$_1$)	12.51 (10.03)	11.77
10.70	π_2 (2b$_1$)	8.96 (10.86)	10.64
13.12	σ_{pyr} (7b$_2$)	9.41 (13.30)	14.79
13.45	π_1 (1b$_1$)	12.93 (12.87)	14.74
14.30	σ_{pyr} (10a$_1$)	13.53 (14.13)	15.98
14.94	σ_{pyr} (6b$_2$)	14.60 (14.48)	16.81
14.94	σ_{pyr}(9a$_1$)	15.29 (15.36)	17.09
15.60	n$_F$	15.52 (16.14)	18.90
17.10	σ_{pyr}(5b$_2$)	17.16 (16.74)	20.39
17.10	σ_F	16.75 (16.41)	19.25
17.90	σ_{pyr}(8a$_1$)	18.46 (17.72)	19.53
(b) 3-Chloropyridine [c]			
9.62 (9.65)	π_3 (1a$_2$)	8.17	9 45
9.85 (9.90)	n$_N$ (11a$_1$)	9.60	11.70
10.50 (10.68)	π_2 (2b$_1$)	9.15	10.61
11.74 (11.82)	σ_{pyr} (7b$_2$)	11.03	12.81
12.50 (12.45)	π_1 (1b$_1$) - π_{Cl}	11.75	13.35
13.35	σ_{pyr} (10a$_1$) - σ_{Cl}	14.71	16.10
13.82	π_1 (1b$_1$) + π_{Cl}	14.30	15.43
13.82	σ_{pyr} (10a$_1$) + σ_{Cl}	12.88	14.55
14.99	σ_{pyr} (6b$_2$)	14.83	16.30
15.90	σ_{pyr} (9a$_1$)	16.39	17.68
16.50	σ_{pyr} (5b$_2$)	16.90	18.58
17.50	σ_{pyr} (8a$_1$)	18.59	19.73
(c) 3-Bromopyridine			
9.38	π_3 (1a$_2$) - π_{Br}	7.89	9.32
9.75	n$_N$ (11a$_1$)	9.34	11.38
10.60	σ_{Br}	10.11	12.01
11.02	π_2 (2b$_1$)	9.06	10.59
11.84	π_3 (1a$_2$) + π_{Br}	10.94	12.58
13.02	π_1 (1b$_1$)	14.11	15.34
13.68	σ_{pyr} (10a$_1$)	12.52	14.11
14.50	σ_{pyr} (7b$_2$)	14.44	15.87
14.50	σ_{pyr} (6b$_2$)	14.62	16.12
15.86	σ_{pyr} (9a$_1$)	16.22	17.51
16.50	σ_{pyr} (5b$_2$)	16.78	18.60
17.50	σ_{pyr} (8a$_1$)	18.48	19.74
(d) 3-Iodopyridine			
8.50	π_3 (1a$_2$) - π_I	7.74	9.08
9.20	n$_N$ (11a$_1$)	9.68	11.68
9.60	σ_I	8.72	10.33
9.85	π_2 (2b$_1$)	9.06	10.47
10.75	π_3 (1a$_2$) + π_I	10.14	11.65
11.80	π_1 (1b$_1$)	14.04	15.19
13.60	σ_{pyr} (7b$_2$)	11.80	13.29
13.60	σ_{pyr} (10a$_1$)	13.98	15.52
14.75	σ_{pyr} (6b$_2$)	14.65	16.10
15.70	σ_{pyr} (9a$_1$)	16.09	17.38
16.30	σ_{pyr} (5b$_2$)	16.76	18.51
17.08	σ_{pyr} (8a$_1$)	18.21	19.66

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

Table 3

Comparison of Experimental Band Intensities and Calculated IE
Distributions for 3-Halopyridines

IE Range (/eV)	Band Intensity Expt [a]	Calculated IE Distribution STO-3G* [b]	6-31G**
(a) 3-Fluoropyridine			
9.12-12.18	3.02	3 (3)	3
12.18-14.05	2.29	3 (2)	—
14.05-16.40	3.92	3 (4)	3
16.40-19.77	2.77	3 (3)	5
(b) 3-Chloropyridine			
9.01-11.35	2.89	4	2
11.35-13.52	3.09	2	3
13.52-15.60	3.25	3	2
15.60-18.38	2.77	2	3
(c) 3-Bromopyridine			
8.90-11.35	4.63	5	2
11.35-13.78	2.53	1	3
13.78-15.91	2.64	3	3
15.91-18.82	2.20	3	3
(d) 3-Iodopyridine			
8.30-10.62	4.23	5	3
10.62-12.94	2.19	1	2
12.94-15.83	3.69	3	3
15.83-19.23	1.89	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.

planar structure and of C_s symmetry, differing mainly by the carbon-halogen bond length, R_{C-X}, and the angle of this bond to the pyridine ring, A_{N-C-X}.

Table 1 compares the optimized values of the critical parameters, with those obtained from STO-3G*//STO-3G* model for 2-halopyridines [15] and with the crystallographic data for the halobenzenes [23]. The maximum deviation of the R_{C-X} bond length between the 3-halopyridines and halobenzenes is 0.03 Å for 3-chloropyridine.

Figure 1 gives the electronic distribution of the 6-31G**//STO-3G* calculations. The nitrogen electronic charge in 3-halopyridines is approximately the same to that of pyridine. 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 π orbitals results in the halogen substituent donating electron density into the ring and so possessing a net positive charge.

Figure 2 gives a schematic of the four lowest occupied MOs obtained from the 6-3 1G**//STO-3G* calculations on pyridine and the 3-halopyridines. For 3-halopyridines this model predicts the n_N IE to be in the 3rd, 3rd, 3rd and 5th positions respectively. Table 2 gives the calculated KA IEs accessible to HeI radiation using HAM/3//STO-3G* (3- 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 3-chloro- and 3-bromopyridine do not differ, whereas for
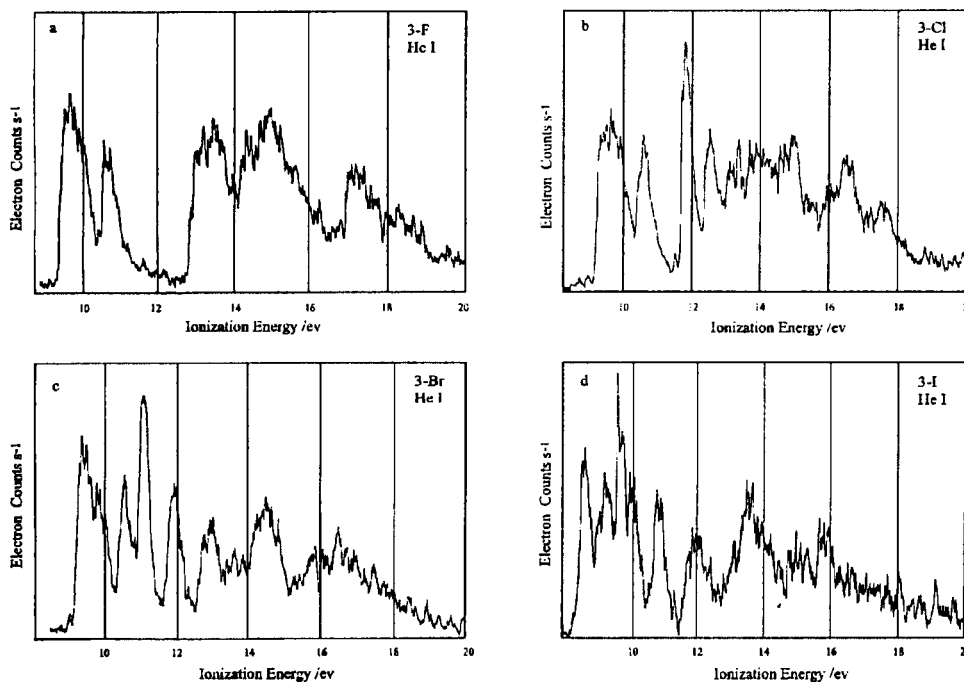

Figure 3. The differential He I spectrum of: (a) 3-fluoropyridine; (b) 3-chloropyridine; (c) 3-bromopyridine; (d) 3-iodopyridine.
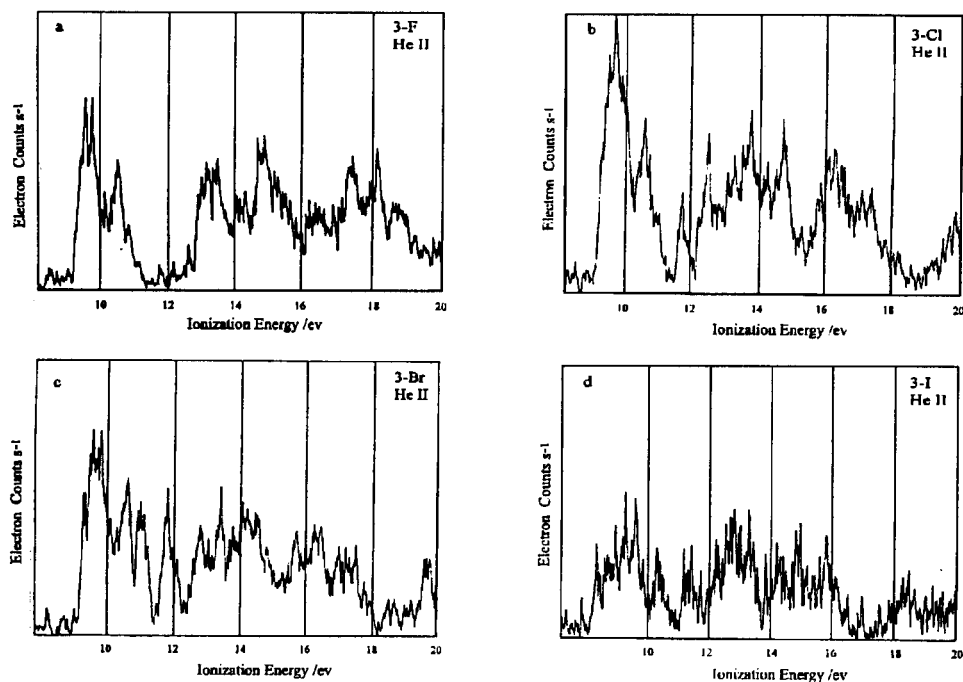
Figure 4. The differential HeII spectrum of: (a) 3-fluoropyridine; (b) 3-chloropyridine; (c) 3-bromopyridine; (d) 3-iodopyridine.

Table 4

Relative HeI and HeII Band Intensities and Percentage Change for 3-Halopyridines.

IE Range (/eV)	Experimental Band Intensities		% Change
	HeI	HeII	
(a) 3-Fluoropyridine			
9.12-12.18	3.02	3.04	0.7
12.18-14.05	2.29	2.09	-8.7
14.05-16.54	3.92	3.34	-14.8
16.54-19.77	2.77	3.53	27.4
(b) 3-Chloropyridine			
9.01-11.35	2.89	4.14	43.3
11.35-13.52	3.09	2.23	-27.8
13.52-15.60	3.25	2.66	-18.2
15.60-18.38	2.77	2.97	7.2
(c) 3-Bromopyridine			
8.90-11.35	4.63	4.38	-5.4
11.35-13.78	2.53	2.83	11.9
13.78-15.91	2.64	2.12	-19.7
15.91-18.82	2.20	2.67	21.4
(d) 3-Iodopyridine			
8.30-10.62	4.23	3.35	-20.8
10.62-12.94	2.19	1.95	-11.0
12.94-15.83	3.69	4.05	9.8
15.83-19.23	1.89	2.65	40.2

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

3-fluoro- and 3-iodopyridine significant differences are evident. For 3-fluoropyridine neither model is in agreement with the HAM/3//STO-3G* calculation.

EXPERIMENTAL

The 3-fluoro-, 3- chloro- and 3-bromopyridine was obtained from Aldrich, but was further purified. The 3-iodopyridine was extremely light sensitive and so it had to be prepared prior to UPS analysis, because it was found to readily decompose. The method used to synthesize 3-iodopyridine was due to Baker, Curtis and Edwards [24]. The resultant product was characterized using both ^{1}H and ^{13}C nmr and the purity was verified from their chemical shifts (which were reported in the literature).

Since all the 3-halopyridines are liquids with relatively high vapour pressures, the gas inlet system of Perkin-Elmer PS 16/18 spectrometer was employed. The spectra of the 3-halopyridines were recorded while they were heated in an oil bath held in a temperature range between 30-40°. Each spectrum was accumulated for over a ~20 minute period and the collection procedure was repeated several times in order to ensure it was reproducible. Furthermore, the spectra were calibrated using butadiene/argon gas mixtures. The operating resolution of the spectrometer was between 25-35 meV. Figure 3 gives the HeI spectra of the 3-halopyridines.

The PS 16/18 spectrometer has been modified to accommodate a Helectros helium lamp and so can also output HeII (40.8 eV) radiation. Under HeI and HeII conditions the photon flux is in the ratio of 10:1 counts per second. The HeII spectra have slightly poorer resolution (due to the trade-off between resolution and sensitivity). The HeII spectra of the 3-halopyridines are given in Figure 4.

The s-p separation rule [25] can be used to predict the number of p-based bands below 18 eV. For halopyridine compounds, the number of bands below 18 eV is given by,

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

where N_C, N_H, N_N and N_X are the number of carbon, hydrogen, nitrogen and halogen atoms respectively. For pyridine, equation (1) predicts 9 p-based bands and, allowing for the well-known cross-over of an s- and p-based band occurring in the 15-18 eV region [10,14-15], a total of 10 bands are expected below ~18 eV. For halopyridines equation (1) predicts 11 p-based bands and with the corresponding cross-over, a total of 12 bands would be predicted below 18 eV. Table 2 gives the twelve experimental vertical IEs for the 3-halopyridines and compares them with other experimentally measured values and calculated KA IE values. The agreement between the measured IEs (where such comparisons can be made [3,9]) is within spectral resolution.

All spectra were digitized for use in the density-of-states analysis [10,14-15]. The density-of-state analysis assumes that the band intensity is directly proportional to orbital degeneracy. That is, where bands are strongly overlapped the total band area in each separable region is directly related to the number of occupied orbitals. Table 3 gives the experimental and calculated band distributions.

As photoionization cross-section varies as a function of photon energy, an effective measure of the variation of band intensity on going from HeI to HeII radiation is given by [10,14-15],

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

A positive (negative) percentage change indicates an enhancement (reduction) on going from HeI to HeII radiation. Table 4 gives the relative HeI and HeII band intensities and their percentage change for the 3-halopyridines.

Discussion

Del Bene [26] has conducted an ab initio study of 2- and 4-mono-substituted pyridines, containing only first row atoms. In particular, her optimized critical parameters (R_{C-F}, A_{N-C-F}) for both 2- and 4- fluoropyridines are (1.35 Å,116°) respectively. These critical parameters are in excellent agreement with the optimized values given in Table 1, indicating that in the case of the fluoropyridines they are insensitive to the position of ring substitution. However, Table 1 clearly indicates that this is not the case for 3-bromo- and 3-iodopyridine. The critical parameters for these molecules more closely resemble those of the halobezenes than those of the 2-halopyridine family [15], indicating that the R_{C-X} and A_{N-C-X} parameters are conversely sensitive to the position of ring substitution. Furthermore, Table 1 also illustrates that the R_{C-X} bond length increases with increasing ionic radii of the halogen substituent.

Figure 1 shows that only the fluorine substituent in this series is sufficiently electronegative to be an effective electron withdrawer (which is also consistent with the calculations of Cain et al [15] and Del Bene [26] on 2-fluoropyridine and Del Bene [26] on 4-fluoropyridine). At first glance, the major difference in the electronic charge distributions between the 2- and 3-halopyridines centres on the carbon atoms at the fifth and sixth ring positions. For 3-halopyridines, the carbon atoms show a net negative and positive electronic charge respectively, while for the

2-halopyridines [15, 26] the reverse trend is evident. However, these trends are consistent with their relative positions to the halogen substituent (ie the carbon atoms, which are meta and para to the halogen substituent show a net negative and positive electronic charge respectively for both series). The net electronic charge on these atoms reflect a delicate balance between inductive and resonance effects of the halogen substituent and the ring nitrogen.

Figure 2 shows the calculated MOs interpreted in terms of a composite-molecule model. That is, the molecule can be defined in terms of two sub-units (a halogen substituent and pyridyl moiety) enabling a composite MO to be obtained from a linear combination of fragment orbitals delocalized over each sub-unit. As a consequence, the composite-molecule model can be constructed from the nine p-based fragment orbitals on the pyridine moiety [6,10,15] and three p-based fragment orbitals of the halogen substituent. Table 2 gives the composite-molecule model description for each KA IE.

In the case of 3-fluoropyridine, the fluorine dominated MOs should be at higher IE than those localized on the pyridyl π sub-unit. However, for the more electron-dense members of the halopyridines the resonance interaction of the np AOs on the halogen substituent with the pyridyl π fragment orbitals results in the halogen substituent donating electron density into the ring. This is consistent with the Pariser- Parr-Pople (PPP) calculations of Martins [27] and with the interpretation of UPS spectra of the halobenzenes [2] and 2-halopyridines [15].

It is evident from Table 2 that for both ab initio models (ie. STO-3G*//STO-3G* and 6-31G**//STO-3G*) the order of the lowest KA IEs is contrary to the accepted assignments of pyridine [6,10], methoxypyridines [10] and 2-halopyridines [15] (the latter two series possessing at least one π band at higher IE than the n_N band). For methoxypyridines, Dunne et al. [10] found that the HAM/3 method correctly assigned the IE sequence for all the isomers, even in cases where more sophisticated ab initio KA models were in error. A similar conclusion was reached for the 2-halopyridine series [15]. Hence total reliance on KA IEs for both the STO-3G*//STO-3G* and 6-3 1G**//STO-3G* models is inappropriate for mono-substituted pyridines [10,14-15].

Table 3 compares the experimental HeI band intensities with the calculated IE distributions using the HAM/3 (3-fluoropridine only), STO-3G*//STO-3G* and 631G**//STO-3G* models. For 3-fluoro-, 3-chloro-, 3-bromo- and 3-iodopyridine the experimental distribution (taking into account analyzer discrimination against slow moving electrons) is (3:2:4:3), (3:3:3:3), (4:3:3:2) and (4:2:4:2) in the respective regions. The shift to a greater density-of-states at lower IE for the more electron-dense members is in accord with the decreasing electronegativity of the halogen substituent. While care needs to be taken in adopting the sequence of KA IEs in total isolation, it would be anticipated that the calculated IE distributions reflect the ability of the models to predict the spread of the IEs. For 3-fluoropyridine the HAM/3//STO-3G* calculation yields the smallest deviation in the spread compared with experiment. This is consistent with previous theoretical studies on methoxypyridines [10] and 2-fluoropyridine [15], where the HAM/3//STO-3G* calculation predicted a better IE distribution than more sophisticated KA/HF models. The 6- 31G*//STO-3G* and STO-3G*//STO-3G* IE distributions are in poor agreement with experiment.

The HAM/3 IE sequence for 3-fluoropyridine is: π_3 (1a$_2$) < n_N (11a$_1$) < π_2 (2b$_1$), which is consistent with the UPS assignment

of 2-fluoropyridine [15] and other monosubstituted pyridines [10]. The introduction of a fluorine substituent results in the "perfluoro" effect (ie. due to the strong inductive effect of fluorine the σ bands are shifted more dramatically to lower IE than the π bands [8]). Assuming that the first two bands are in accordance with the HAM/3//STO-3G* calculation then the UPS spectrum of 3-fluoropyridine suggests that the shift from pyridine π and σ bands is of the order ~0.1 and 0.8 eV respectively (which is in keeping with the "perfluoro" effect in the UPS of 2-fluoropyridine, where the shifts were 0.3 and 0.8 eV respectively [15] and with shifts in other aromatic compounds [2]).

In a number of molecules the fluorine lone-pair is typically located at ~16 eV [2]. For the 3-fluoropyridine Table 4 shows there is a sizeable reduction on going from HeI to HeII radiation in the region 14-16 eV. In particular, the band at 15.60 eV reduces its intensity dramatically. Its percentage change on going from HeI to HeII radiation is in keeping with ionization from a fluorine lone-pair (n_F). The σ_F band is assigned at 17.10 eV. The region between 16-20 eV shows an intensity enhancement, which is due to the presence of an additional three pyridyl based bands in this region. Simple correlations with the accepted assignment of pyridine [6, 10] and 2-fluoropyridine [8, 15], the "perfluoro" effect, HAM/3//STO-3G* calculations and HeI/HeII band intensity comparisons substantiate the preferred composite-molecule model assignment given in Table 2.

For 3-chloropyridine the HeI/HeII ratios indicate an intensity enhancement occurs in the 9-11 eV region on going from HeI to HeII radiation (which is consistent with ionization arising from MOs composed mainly of C, N and H character). The preferred assignment in this region is: π_3 ($1a_2$) < n_N ($11a_1$) < π_2 ($2b_1$). A dramatic reduction in intensity would indicate the presence of chlorine character in the MO. Such a reduction is shown in the 11.4-13.5 eV region, a region where the chlorine lone-pairs are typically assigned for a number of compounds [2,15]. The preferred composite-molecule assignment of 3-chloropyridine is given in Table 2. This assignment is also consistent with the order of the first four IEs assigned by and Murrell and Suffolk [3] and Modelli and Distefano [9] (which was constructed from their HeI study of all three isomers of chloropyridines) and with the HeI/HeII assignment of 2-fluoropyridine by Cain et al [15].

For a number of compounds the bromine lone-pair orbitals were assigned in a region around 10.5 eV [2]. The π symmetry bromine lone-pair orbitals significantly interact with the π_3 of the pyridyl moiety. The in-plane bromine lone-pair is of σ symmetry and so is relatively unshifted from its molecular value at 10.5 eV and therefore is assigned at 10.6 eV. The HeI/HeII study confirms this assignment, since in the 9.011.4 eV region there is a small reduction in band intensity (i.e. -5% as compared with a 43% enhancement for 3-chloropyridine) on going from HeI to HeII radiation. This is consistent with ionization from MOs composed mainly of C, N, H character, but with a Br AO presence. In the 10-12 eV region significant reduction occurs (see Figures 3 and 4), which indicates the presence of bromine character in the MO. These observations together with using simple correlation of the four lowest energy IEs of 2-bromopyridine [15], yields the sequence for 3-bromopyridine IEs as: π_3 ($1b_1$) - π_{Br} < n_N ($11a_1$) < σ_{Br} < π_2 ($2b_1$). The preferred assignment is given in Table 2.

For a number of molecules the iodine lone-pairs are typically located ~9.9 eV [2]. As the lowest π IE for pyridine is at 9.60 eV, significant resonate interaction can occur with the lowest π

bands of the iodine substituent. The in-plane iodine lone-pair is of σ symmetry and so remains relatively unshifted from its molecular value at 9.9 eV and so is assigned at 9.60 eV. The HeI/HeII ratios confirm its location, since in the 8.3-10.6 eV region there is a reduction of some 20% in band intensity on going from HeI to HeII radiation, which is consistent with ionization from MOs composed mainly of iodine character. Using simple correlation with the lowest energy IEs of 2-iodopyridine [15], the preferred IE sequence for 3-iodopyridine is: π_3 ($1a_2$) - π_I < n_N ($11a_1$) < σ_1 < π_2 ($2b_1$). The composite-molecule model assignment is given in Table 2.

Conclusion.

The UPS spectra of 3-halopyridines can be interpreted using a composite-molecule model which is based on linear combination of fragment orbitals localized on the pyridyl moiety and on the halogen substituent. The sequence for the four lowest ionization energies of the 3-fluoro- and 3-chloropyridine is: π_3 ($1a_2$) < n_N ($11a_1$) < π_2 ($2b_1$) < σ_{pyr} ($7b_2$), whereas for 2-bromo- and 2-iodopyridine the assignment is: π_3 ($1a_2$) - π_X < n_N ($11a_1$) < σ_X < π_2 ($2b_1$). Comparison of the HeI/HeII band intensities ratios, simple correlations with pyridine [6], 2-halopyridine series [15], with other mono-substituted pyridines [10] and (in the case of 2-fluoropyridine) HAM/3//STO-3G* calculations confirmed these assignments. 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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