

## Perfluoro Effect in Photoelectron Spectroscopy. II. Aromatic Molecules

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**Abstract:** The  $\pi$  ionization potentials of planar aromatic systems and their perfluoro derivatives are very nearly equal, whereas the  $\sigma$  ionization potentials in the perfluoro compounds are several electron volts larger than in the perhydro compound (the perfluoro effect). Comparisons of the high-resolution photoelectron spectra of benzene, pyridine, *s*-triazine, borazine, *p*-benzoquinone, and naphthalene with those of their perfluoro derivatives lead to the following conclusions. (a) In benzene, the orbital ordering is  $\pi_3$ ,  $\pi_2$  ( $1e_{1g}$ , 9.421 eV),  $\sigma$  ( $3e_{2g}$ , 11.49 eV),  $\pi_1$  ( $1a_{2u}$ , 12.3 eV), while in hexafluorobenzene the ordering of  $\sigma$  and  $\pi_1$  is reversed. (b) The lone-pair and  $\pi_3$  MO's of pyridine are nearly degenerate (9.67 and 9.80 eV), and their order cannot be deduced. These two MO's are followed by  $\pi_2$  (10.5 eV) and a  $\sigma$  MO at 12.45 eV which is a component of the  $3e_{2g}$  MO's of benzene. In pentafluoropyridine, the ordering is  $\pi_3$ ,  $\pi_2$ ,  $\sigma$ ,  $\pi_1$ . (c) The  $\pi_3$ ,  $\pi_2$  MO's of *s*-triazine show a slight Jahn-Teller split (11.71 and 12.15 eV), and are followed by the  $e'$  (10.41 eV) and  $a_1'$  (13.25 eV) combinations of the nitrogen lone-pair AO's.  $\pi_1$  of *s*-triazine comes at 14.65 eV. In cyanuric fluoride,  $C_3N_3F_3$ ,  $\pi_3$ ,  $\pi_2$  are similarly split by 0.4 eV, and the  $\pi_1$  ionization precedes those from the lone pairs. (d) The uppermost MO's of borazine are  $\pi_3$ ,  $\pi_2$  rather than  $\sigma$  as suggested by other workers, and these are followed by  $\sigma$  and  $\pi_1$ , as in benzene. (e) The first four ionizations in naphthalene are out of  $\pi$  MO's, the fifth out of a  $\sigma$  MO.

In the first part of this work,<sup>1</sup> it was established that upon substitution of the hydrogen atoms of a planar nonaromatic molecule by fluorine atoms, the  $\sigma$  MO's of the molecule are stabilized by 2–3 eV, in contrast to the  $\pi$  MO's, which are an order of magnitude less stabilized. The specific stabilizing effect on the  $\sigma$  MO's, termed the "perfluoro effect," was not observed in grossly nonplanar systems (but see hexafluorobutadiene<sup>1</sup>) such as those containing the methyl group, for in these the  $\pi$ - $\sigma$  distinction can no longer be made and all MO's are approximately equally stabilized by the substitution. In the work on nonaromatic systems, the successive ionization potentials were determined using photoelectron spectroscopy and then assigned to MO's using Gaussian type orbital (GTO) calculations and Koopmans' theorem. Once identified, the transitions in the perhydro and perfluoro molecules were correlated using overlap and atomic population analyses. In the present paper, we wish to apply the perfluoro effect to the assignments of photoelectron bands in planar aromatic molecules which are too large for high-quality GTO calculations. Consequently, the interpretations will be more intuitive and will depend totally upon the validity of the perfluoro effect in distinguishing  $\pi$  and  $\sigma$  MO's. As will be seen, this approach leads to a reasonable assignment of the bands, and in a small way justifies the validity of the perfluoro effect in this type of compound. Since the region between 15 and 20 eV in a perfluorinated molecule as small as  $F_2C=CF_2$  is undecipherable, even with GTO calculations, there is no hope for a detailed assignment in this region for the much larger molecules studied here. However, where the He(II) spectra provide data beyond 20 eV, the perhydro-perfluoro correlations are again recognizable and assignments can be made.

The six pairs of molecules considered here are benzene-hexafluorobenzene, pyridine-pentafluoropyridine, *p*-benzoquinone-tetrafluoro-*p*-benzoquinone, *s*-triazine-cyanuric fluoride, borazine-*B*-trifluoroborazine,

(1) C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Amer. Chem. Soc.*, **94**, 1451 (1972).

and naphthalene-octafluoronaphthalene. All were commercial products further purified by gas-phase chromatography or recrystallization. The experimental technique is described in part I.

The present investigation has special relevance, since the photoelectron spectra of benzene, pyridine, and naphthalene have been recorded in the past, but in each case there is a conflict over which of the transitions proceed from  $\pi$  MO's and which proceed from  $\sigma$  MO's. In addition, Bralsford, *et al.*,<sup>2</sup> in an earlier photoionization study, reported that the behaviors of the  $\pi$  ionization potentials of ethylene and benzene on perfluorination were markedly different and then went on to explain how the effects of perfluorination of aromatics such as benzene are essentially different from the effects of perfluorination of nonaromatics such as ethylene. On the contrary, there is nothing in the present work which suggests that the perfluoro effect operates any differently in the two classes of molecules.

### Results

**Benzene-Hexafluorobenzene.** The photoelectron spectra of benzene and hexafluorobenzene are compared in Figure 1, and the pertinent ionization energies and vibrational frequencies are tabulated in Table I. The benzene data are a compilation of those of Åsbrink, *et al.*,<sup>3,4</sup> and of Turner, *et al.*<sup>5</sup> It has been claimed by some<sup>6</sup> that two additional ionizations lie between the 9.24- and 11.49-eV bands of benzene, but there is strong evidence against this,<sup>3,7,8</sup> and we concur with the view that the additional bands are spurious. The orbital

(2) R. Bralsford, P. V. Harris, and W. C. Price, *Proc. Roy. Soc.*, **258**, 459 (1960).

(3) L. Åsbrink, E. Lindholm, and O. Edqvist, *Chem. Phys. Lett.*, **5**, 609 (1970).

(4) L. Åsbrink, O. Edqvist, E. Lindholm, and L. E. Selin, *ibid.*, **5**, 192 (1970).

(5) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley, London, 1970.

(6) P. Natalis, J. E. Collin, and J. Momigny, *Int. J. Mass Spectrom. Ion. Phys.*, **1**, 327 (1968).

(7) A. D. Baker, C. R. Brundle, and D. W. Turner, *ibid.*, **1**, 443 (1968).

(8) J. A. R. Samson, *Chem. Phys. Lett.*, **4**, 257 (1969).

Table I. Ionization Potentials in the Benzene-Hexafluorobenzene Pair

Benzene <sup>a</sup>			Hexafluorobenzene		
Adiabatic	Vertical	Vibration	Adiabatic	Vertical	Vibration
9.241	9.241	685 ( $\nu_{18}'$ ), 984 ( $\nu_2'$ ), 1290 ( $\nu_{17}'$ )	9.93 (6)	10.12 (0)	1450 ( $\nu_1'$ ), 400 ( $\nu_2'$ )
11.490	11.490	645 ( $\nu_{18}'$ ), 1290 ( $\nu_{17}'$ )	12.58 (1)	12.77 (1)	1550 ( $\nu_1'$ ?), 530 ( $\nu_2'$ )
	12.3		13.84 (4)	14.02 (4)	1450 ( $\nu_1'$ )
13.8	13.8				
14.7	14.7				
15.4	15.4	2340 ( $\nu_1'$ )	14.75 (1)	14.75 (1)	1550 ( $\nu_1'$ ?), 480 ( $\nu_2'$ )
16.85 <sup>b</sup>	16.85 <sup>b</sup>	927 ( $\nu_2'$ )	15.82	15.82	
18.7	19.2			16.3	
22.2	22.8			16.6 (?)	
	28.8			17.6	
				18.6	
			ca. 19.8	20.3	
			ca. 21.8	22.4	
				25.5	

<sup>a</sup> Values taken from ref 3-5. <sup>b</sup> This value is reported as 16.99 eV in ref 3, but we have carefully remeasured it and find  $16.85 \pm 0.01$  eV.

assignments in Figure 1 are those of Åsbrink, *et al.*,<sup>4</sup> based in part on the assumption that the integrated intensities in the He(II) spectrum are proportional to the orbital degeneracies of the ionized MO's. Though we have repeatedly found this to be a poor approximation,<sup>9</sup> we accept the proposed assignments. Special attention will be given to the bands in the 9-14- and 19-26-eV regions in both compounds. A low-resolution photoelectron study of hexafluorobenzene has been reported by Clark and Frost,<sup>10</sup> and Caldow has semiempirically calculated the ionization potentials.<sup>11</sup>

Since the photoelectron spectrum of benzene is comparatively well understood, while that of hexafluorobenzene is not, the perfluoro effect can be used to advantage in understanding the orbital ordering in the latter compound.

The uppermost orbital in benzene is the doubly degenerate  $\pi_3, \pi_2$  ( $1e_{1g}$ ) MO having an ionization potential of 9.241 eV. The corresponding ionization in hexafluorobenzene comes at 10.12 eV, with a resulting  $\pi$  shift of 0.88 eV when compared with benzene. This shift is at the upper end of the range of  $\pi$  MO shifts which were observed in nonaromatic compounds,<sup>1</sup> but, as will be seen, is not at all unusual for aromatic compounds. In the high-resolution photoelectron spectrum of benzene, there is evidence for the excitation of nontotally symmetric vibrations in the 9.241-eV band, symptomatic of Jahn-Teller distortion.<sup>5</sup> In hexafluorobenzene, we find vibrational intervals of 1450 and 400  $\text{cm}^{-1}$  excited which are tentatively assigned to the totally symmetric modes  $\nu_1'$  and  $\nu_2'$ , respectively. The corresponding neutral molecule frequencies are 1488 and 559  $\text{cm}^{-1}$ . In hexafluorobenzene,  $\nu_1$  is the C-F stretch and  $\nu_2$  is a ring breathing mode. These are the only totally symmetric motions in the molecule.<sup>12</sup>

The second and third ionizations in benzene appear as a badly overlapped pair of bands with vertical ionization potentials of 11.49 and 12.3 eV. Earlier experimental work was interpreted as showing that the band at 11.49 eV corresponded to ionization from the second  $\pi$  MO,  $\pi_1$  ( $1a_{2u}$ ),<sup>11,13</sup> whereas later theoretical work placed the ionization from the  $3e_{2g}$   $\sigma$  MO at 11.49 eV

and that from  $\pi_1$  at 12.3 eV.<sup>14</sup> In accord with the  $\pi, \sigma, \pi$  ordering, Åsbrink, *et al.*,<sup>4</sup> point out that the photoelectron intensities imply that the first two ionizations are from doubly degenerate MO's, but the third is from a nondegenerate MO. While we do not consider the

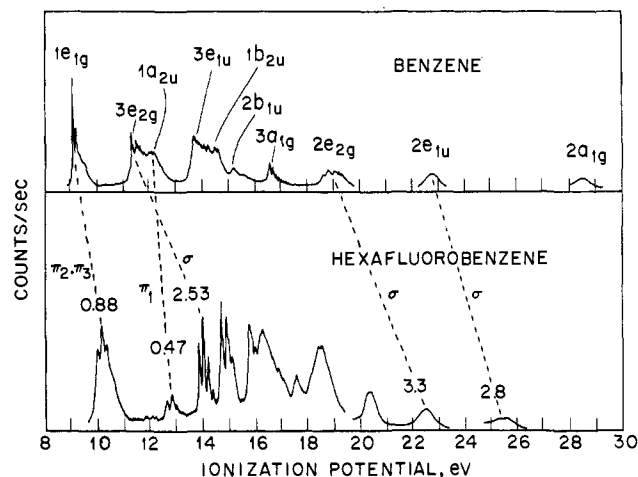


Figure 1. Correlation of the photoelectron bands of benzene (upper) and of hexafluorobenzene (lower).

intensity argument to be a very good one, the ordering so derived does lead to a reasonable set of perfluoro shifts. Thus the 12.3-eV ( $\pi_1, 1a_{2u}$ ) band of benzene appears as the 12.77-eV band of hexafluorobenzene, the perfluoro shift being less than 0.5 eV. By contrast, the  $3e_{2g}$   $\sigma$  level of benzene (11.49 eV) appears at 14.02 eV in hexafluorobenzene, the perfluoro shift being five times as large. Though not quantitative, the relative intensities of the first three bands of hexafluorobenzene, Figure 1, also suggest that the second and third bands of benzene have crossed over in hexafluorobenzene. However, such intensity arguments are frequently erroneous. The  $1e_{1g}$   $\pi, 3e_{2g}$   $\sigma, 1a_{2u}$   $\pi$  ordering deduced for benzene using the perfluoro effect has recently been obtained theoretically in a Gaussian orbital calculation.<sup>15</sup>

(14) See, for example, J. M. Schulman and J. W. Moskowitz, *J. Chem. Phys.*, **43**, 3287 (1965).

(15) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **19**, 1 (1970).

(9) See, for example, C. R. Brundle, N. A. Kuebler, M. B. Robin, and H. Basch, *Inorg. Chem.*, **11**, 20 (1972).

(10) I. D. Clark and D. C. Frost, *J. Amer. Chem. Soc.*, **89**, 244 (1967).

(11) G. L. Caldow, *Chem. Phys. Lett.*, **2**, 88 (1968).

(12) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1947 (1963).

(13) A. D. Baker and D. W. Turner, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 131 (1970).

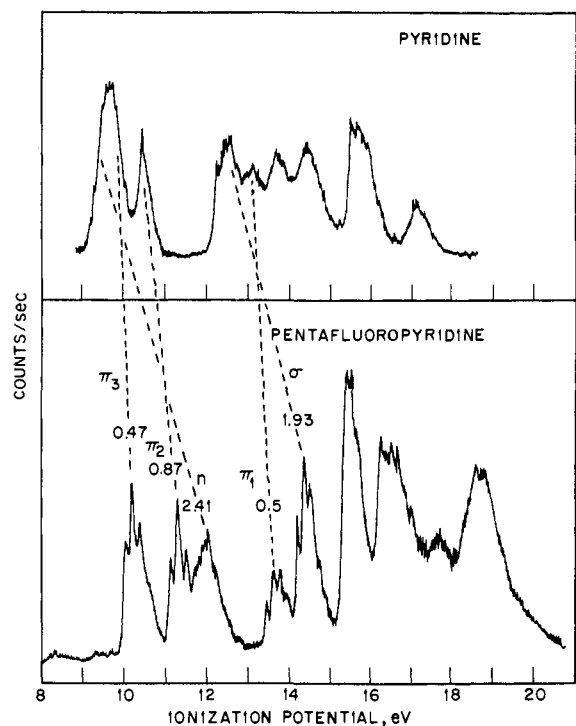


Figure 2. Correlation of the photoelectron bands of pyridine (upper) and of pentafluoropyridine (lower).

Trying to trace the benzene levels to their final resting place in hexafluorobenzene in the 14–19-eV region is an impossibility, since this region in hexafluorobenzene also contains 12 “fluorine lone-pair” ionizations in addition to the analogs of the original benzene transitions. This additional ionization due to the lone pairs on the fluorine atoms manifests itself as the large block of increased ionization in the 16–19-eV region, Figure 1. The term lone pair as applied to the 2p electrons of the fluorine atoms is probably something of a misnomer, as it appears that they are strongly involved in C–F bonding, unlike the corresponding electron pairs in chloro, bromo, and iodo compounds.<sup>1,16</sup> Once beyond the 19-eV mark, the benzene–hexafluorobenzene correlation can be picked up again. The two bands at 19.1 and 22.7 eV in benzene are assigned by Åsbrink, *et al.*, as coming from the  $2e_{2g}$  and  $2e_{1u}$   $\sigma$  MO’s, both of which are composed largely of 2s AO’s on carbon. The corresponding bands in hexafluorobenzene appear at 22.4 and 25.5 eV, respectively, in the He(II) spectrum, with resultant  $\sigma$  perfluoro shifts of 3.3 and 2.8 eV. A third level of this sort in benzene ( $2a_{1g}$ ) is observed at 28.7 eV and should appear at 31.5–32.5 eV in hexafluorobenzene. We cannot locate ionization potentials which are as high as this with our apparatus, but it could readily be seen using the ESCA technique.

In each of the first four bands of hexafluorobenzene, the excitation of a  $1450\text{--}1550\text{-cm}^{-1}$  vibration is prominent, which appears to be  $\nu_1'$ , the totally symmetric C–F stretch. By contrast, the  $\pi_2$ ,  $\pi_3$  ionization from benzene shows no C–H vibrational excitation, though this appears in higher  $\sigma$  ionizations.

The relative intensities of the bands of the benzene spectrum under He(I) and He(II) excitation are nearly

(16) C. R. Brundle, M. B. Robin, and H. Basch, *J. Chem. Phys.*, **53**, 2196 (1970).

identical, but in hexafluorobenzene, the band at 16.3 eV is considerably stronger in the He(II) spectrum.

**Pyridine–Pentafluoropyridine.** The situation in pyridine is rather like that in benzene, only more so. In pyridine, the doubly degenerate  $\pi$  orbitals of benzene are split into two components, the nitrogen lone-pair ionization intrudes at low energy, and the  $1a_{2u}$ ,  $3e_{2g}$  complex of benzene becomes three levels in pyridine. We believe the perfluoro effect can give a relatively unambiguous assignment of this myriad of levels in pyridine, if one will accept the validity of small  $\pi$  shifts and large  $\sigma$  shifts on perfluorination.

The question of the ordering of the various MO’s of pyridine has been of great interest for several years. A study of Rydberg series in the optical spectrum of pyridine led El Sayed, *et al.*,<sup>17</sup> to postulate  $\pi$  ionization potentials at 9.266 and 11.56 eV, and the nonbonding ionization potential at about 10.3 eV. Jonsson, *et al.*,<sup>18</sup> argue instead for a  $\pi$ ,  $\pi$ , n ordering, following studies of the electron-scattering spectrum and theoretical calculations. GTO calculations by Clementi group the first three levels quite closely, the figures being  $\pi_3$  (12.2 eV),  $\pi_2$  (12.5 eV), and n (12.7 eV).<sup>19</sup> The semiempirical calculation of Dewar and Worley placed the  $\pi_3$  level at 9.65 eV and the n level at 9.66 eV.<sup>20</sup>

The photoelectron spectrum of pyridine, Figure 2, shows a broad feature with an adiabatic ionization potential of 9.26 eV, followed by three bands at 10.50, 12.45, and 12.6 eV. On looking closer at the 9.26-eV band, Figure 3f, it is seen that there are two ionizations present,<sup>13</sup> the two vertical ionization potentials being 9.67 and 9.80 eV.<sup>6</sup> In the early photoelectron work on assigning the ordering of the pyridine MO’s,  $\pi_3$ ,  $\pi_2$ , n was suggested as the most likely assignment, but with the possibility of  $\pi_3$ , n,  $\pi_2$  admitted.<sup>5,13</sup> This was based in part on the effect of ring substitution on the first ionization potential. Later work involving the substitution of a trimethylsilyl group onto the ring showed that the ordering was not  $\pi_3$ ,  $\pi_2$ , n.<sup>21</sup> This was supported by work which showed that the degenerate  $\pi_3$ ,  $\pi_2$  levels of benzene were split by about 1 eV on substitution of a nitrogen into the ring;<sup>22</sup> hence, the first two bands in the photoelectron spectrum of pyridine (0.13 eV split) cannot be  $\pi_3$ ,  $\pi_2$ . In a practical sense, the extreme closeness of the first two ionization potentials makes the determination of their orbital ordering extremely difficult. If Rydberg transitions from these orbitals can be found in the optical spectrum, the 0.13-eV splitting should be visible, and presumably a high-resolution rotational analysis would be able to show the polarization direction for each component, thereby indicating the symmetries of the originating MO’s. Gleiter, *et al.*,<sup>23</sup> take the view that n precedes  $\pi_3$ , though it is difficult to see how they can be sure of this. We will assume that Gleiter, *et al.*, are correct for the sake of continuing our discussion of the perfluoro effect,

(17) M. F. A. El Sayed, M. Kasha, and Y. Tanaka, *J. Chem. Phys.*, **34**, 334 (1961).

(18) B.-Ö. Jonsson, E. Lindholm, and A. Skerbele, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 385 (1969).

(19) E. Clementi, *J. Chem. Phys.*, **46**, 4731 (1967).

(20) M. J. S. Dewar and S. D. Worley, *ibid.*, **51**, 263 (1969).

(21) E. Heilbronner, V. Hornung, H. Bock, and H. Alt, *Angew. Chem. Int. Ed., Engl.*, **8**, 524 (1969).

(22) A. D. Baker, D. Betteridge, N. R. Kemp, and R. E. Kirby, *Chem. Commun.*, 286 (1970).

(23) R. Gleiter, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **9**, 901 (1970).

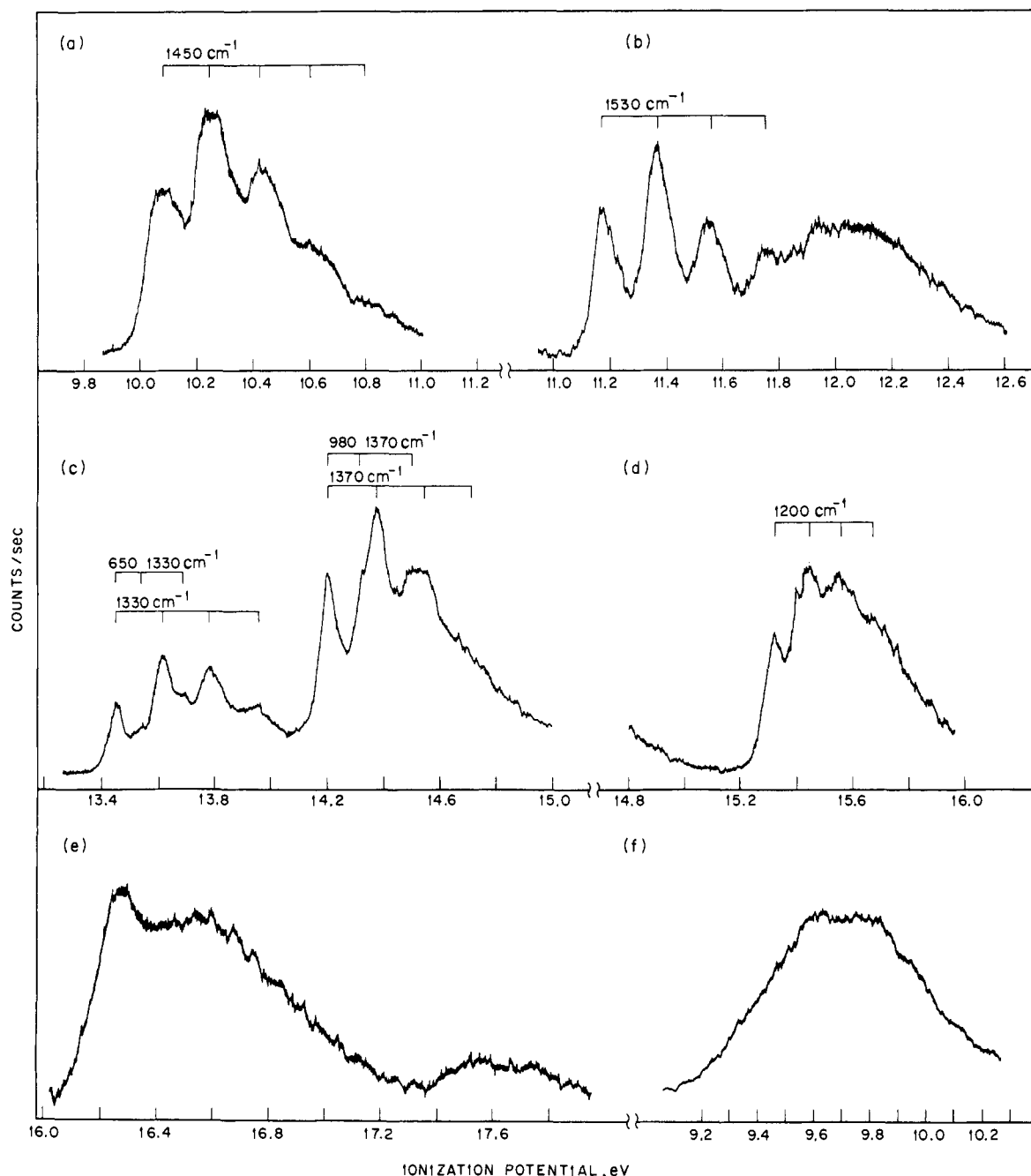


Figure 3. Details of the vibronic structure in the bands of pentafluoropyridine (a-e) and pyridine (f).

though it is largely immaterial to our argument, since the two levels are so close.

Comparing the photoelectron spectra of pyridine and pentafluoropyridine, Figure 2, we see first of all that the difference in  $\pi$  and  $\sigma$  shifts on perfluorination has lifted the accidental near-degeneracy of the  $n$  and  $\pi_3$  MO's in pentafluoropyridine;  $\pi_3$  and  $\pi_2$ , which are found at 9.80 and 10.50 eV in pyridine, appear as two very similar looking bands at 10.27 and 11.37 eV in pentafluoropyridine, whereas the 9.67-eV band ( $n$  of pyridine) is shifted to 12.08 eV in the pentafluoro derivative. Assigned this way, the  $\pi_3$ ,  $\pi_2$   $\pi$  shifts are 0.47 and 0.87 eV, whereas the  $n$  orbital is shifted by 2.41 eV. One can go one step further by assigning the 12.45-eV band of pyridine to a  $\sigma$  MO (derived from the  $3e_{2g}$  set of benzene) which moves to 14.38 eV in pentafluoropyridine (1.93-eV  $\sigma$  shift), while the  $\pi_1$  MO of pyridine

(13.1 eV) suffers a smaller shift of 0.5 eV in moving to 13.62 eV in the pentafluoro derivative. Though there is no independent evidence for the assignments proposed here for the pyridine-pentafluoropyridine pair, the resultant shifts are quite similar to those proposed for the benzene-hexafluorobenzene and naphthalene-octafluoronaphthalene pairs.

Because of the large number of vibrations in pentafluoropyridine and the moderate resolution of its vibronic structure, Figure 3a-e, it is difficult to specify the vibrational modes in the ionic states with any certainty. According to Long and coworkers,<sup>24,25</sup> the totally symmetric ground-state vibrations at 1650 ( $\nu_1''$ ), 1529 ( $\nu_2''$ ), and 1404  $\text{cm}^{-1}$  ( $\nu_3''$ ) are described as mixtures of

(24) D. A. Long and R. T. Bailey, *Trans. Faraday Soc.*, **59**, 599 (1963).

(25) D. A. Long and D. Steele, *Spectrochim. Acta*, **19**, 1791 (1963).

Table II. Ionization Potentials in the Pyridine–Pentafluoropyridine Pair

Pyridine <sup>a</sup>			Pentafluoropyridine		
Adiabatic	Vertical	Vibration	Adiabatic	Vertical	Vibration
9.25	9.67	560 ( $\nu_9'$ ?)	10.08	10.27	1450 ( $\nu_1'$ ?)
	9.80		11.17	11.37	1530 ( $\nu_1'$ ?)
10.42	10.50	1650 ( $\nu_4'$ ?), 560 ( $\nu_9'$ ?)		12.08	
12.27	12.45		13.46	13.62	1330 ( $\nu_1'$ ?, $\nu_3'$ ?), 650 (?) ( $\nu_6'$ ?)
	12.6		14.20	14.38	1370 ( $\nu_1'$ ?), 980 (?)
	13.1		15.32	15.45	1200 ( $\nu_1'$ ?)
	13.8		ca. 16.04	16.27	
	14.5		ca. 17.3	17.6	
15.6	15.6		ca. 18.0	18.6	
	17.1		ca. 19.8	20.5	
			ca. 21.7	22.2	
				22.7	

<sup>a</sup> Taken from ref 5.

ring stretching and C–F stretching motions, with the first two being largely ring stretching and  $\nu_3$  being largely C–F stretching. These vibrations are seen in several of the ionic states as well, Table II and Figure 3,

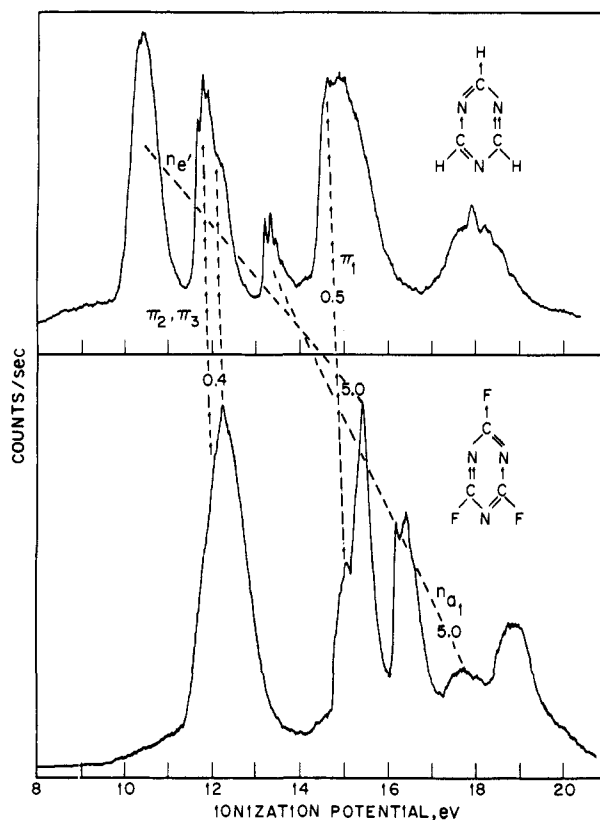
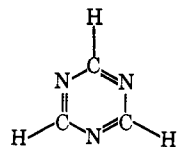


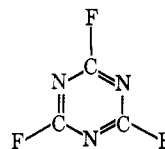
Figure 4. Correlation of the photoelectron bands of *s*-triazine (upper) and of cyanuric fluoride (lower).

with values in the 1200–1500-cm<sup>-1</sup> range. The 1530-cm<sup>-1</sup> interval in the 11.37-eV band is probably  $\nu_1'$ , whereas the 1450-cm<sup>-1</sup> vibration in the 10.27-eV band could be either  $\nu_1'$  or  $\nu_2'$ , and values of 1200–1400 cm<sup>-1</sup> could be any one of  $\nu_1'$ ,  $\nu_2'$ , or  $\nu_3'$ . The vibronic structures of the pyridine bands are illustrated in ref 5.

***s*-Triazine–Cyanuric Fluoride.** The problem of the assignment of the MO's in *s*-triazine



is somewhat like that of pyridine, except that  $\pi_2$  and  $\pi_3$  are again degenerate in the triazine, and there are three “lone pair” orbitals to be assigned instead of one. Spectra of *s*-triazine and its perfluoro analog, cyanuric fluoride



are shown in Figures 4–6, and the spectral data are tabulated in Table III. Application of the perfluoro-shift rule quickly identifies the bands at 10.41 and 13.25 eV in *s*-triazine as being ionizations from  $\sigma$  MO's, since there are no corresponding bands within 1 eV of these energies in the spectrum of cyanuric fluoride. In fact, it seems most likely that the two bands at 10.41 and 13.25 eV are due to ionization from the  $e'$  and  $a_1'$  lone-pair MO's. Of course, the large splitting between these MO's argues that they are not nonbonding, as might otherwise be thought. Simple considerations show that the  $e'$ – $a_1'$  splitting in *s*-triazine should be 1.5 times as large as that in



which is 1.50 eV.<sup>23</sup> The predicted value of 2.25 eV is in adequate agreement with the value of 2.84 eV proposed here for the lone-pair splitting in *s*-triazine. The 13.25-eV band shows a rather vertical progression of 1190 cm<sup>-1</sup>, which is probably assignable as  $\nu_2'$ , a totally symmetric ring breathing mode having a frequency of 1132 cm<sup>-1</sup> in the ground state.<sup>26</sup>

Having found the nonbonding orbitals in *s*-triazine, it is natural then to assign the  $\pi_2$ ,  $\pi_3$  sets as the split band having maxima at 11.71 and 12.15 eV in *s*-triazine, and the split band having maxima at 11.9 and 12.3 eV in the fluoride. The separations of 0.4 eV are plausibly ascribed to Jahn–Teller effects, but it is odd that they are so much smaller than this in benzene and hexafluorobenzene. Alternatively, it is possible that the 11.71-eV band of *s*-triazine is a transition from the  $\pi_2$ ,  $\pi_3$  levels with a negligible Jahn–Teller splitting, and that the 12.15-eV component is a  $\sigma$  MO ionization. We will say more about this below.

(26) J. E. Lancaster, R. F. Stamm, and N. B. Colthup, *Spectrochim. Acta*, **17**, 155 (1961).

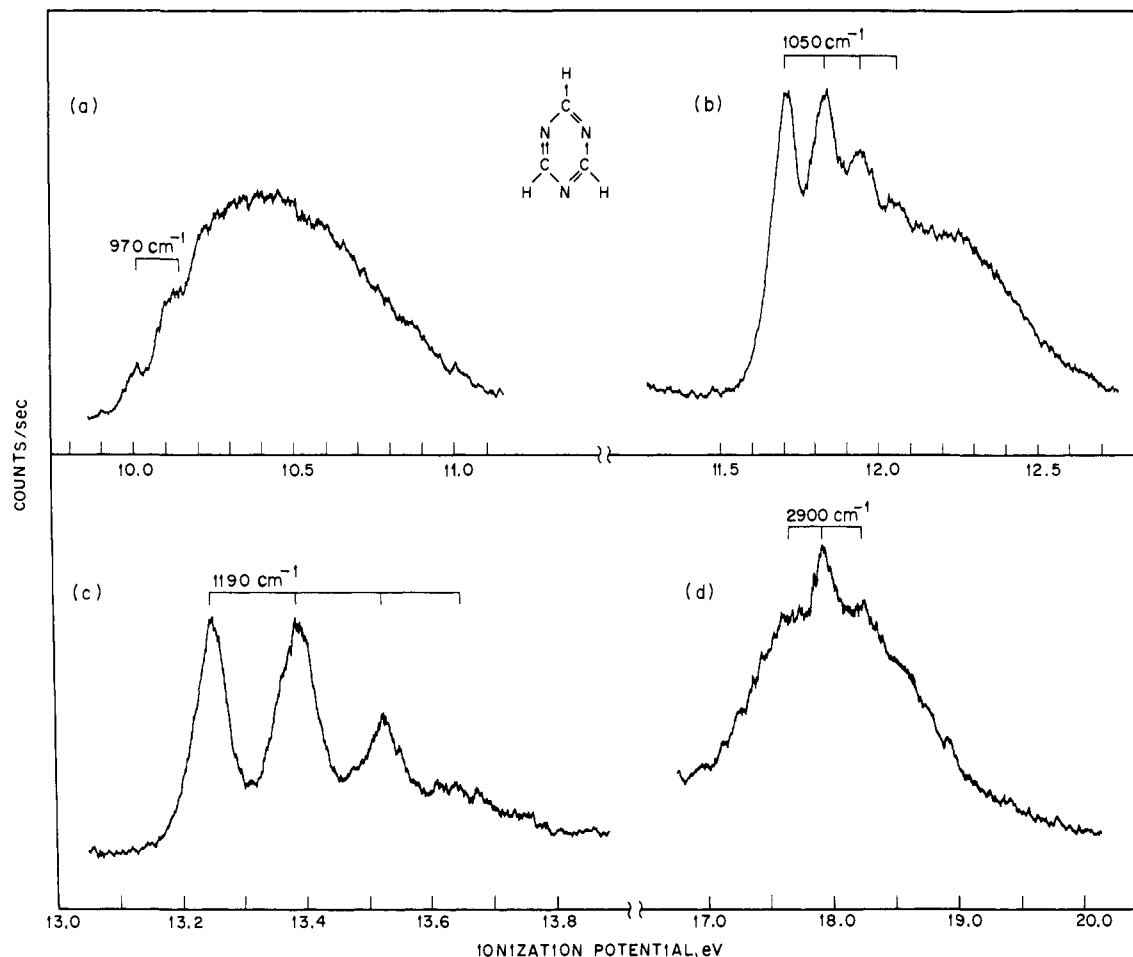


Figure 5. Details of the vibronic structure in the bands of *s*-triazine.

In *s*-triazine, the 11.71-eV component of the  $\pi_2$ ,  $\pi_3$  band shows the excitation of at least 4 quanta of *ca.* 1050  $\text{cm}^{-1}$ , which can be assigned to  $\nu_2'$ . In cyanuric fluoride, the second component with an apparent origin

respectively. A similar set of numbers results if we take the  $\pi_1$  MO of *s*-triazine at 14.65 eV and that of cyanuric fluoride at about 15 eV, Figure 4. In this case, the  $\pi$  shift on perfluorination is less than 0.5 eV.

Table III. Ionization Potentials in the *s*-Triazine–Cyanuric Fluoride Pair

<i>s</i> -Triazine			Cyanuric Fluoride		
Adiabatic	Vertical	Vibration	Adiabatic	Vertical	Vibration
10.1	10.41	970 ( $\nu_2'$ )	11.5	12.0	
11.71	11.71	1050 ( $\nu_2'$ )		12.34	1370 ( $\nu_1'$ )
	12.2				
13.25	13.25	1190 ( $\nu_2'$ )	14.87	15.12	1000 ( $\nu_1'$ )
14.4	14.65		15.4	15.53	1000 ( $\nu_1'$ )
	14.85		16.25	16.25	1000 ( $\nu_1'$ )
17.7	17.94	2900 ( $\nu_1'$ )			
	22.3				

at 12.15 eV also displays 4 quanta of *ca.* 1370  $\text{cm}^{-1}$ , which is most likely  $\nu_1'$ , the totally symmetric C–F stretch ( $\nu_1'' = 1496 \text{ cm}^{-1}$ ).<sup>27</sup> Since the totally symmetric ring breathing motions in cyanuric fluoride have frequencies of 999 and 642  $\text{cm}^{-1}$  in the ground state, it seems once again that ring deformation motions are excited in the perhydro ionizations, but C–F stretching is excited in the corresponding perfluoro ionizations.

In benzene and hexafluorobenzene, the separations between the  $\pi_1$  and the  $\pi_2$ ,  $\pi_3$  MO's are 3.1 and 2.65 eV,

(27) J. E. Griffiths and D. E. Irish, *Can. J. Chem.*, **42**, 690 (1964).

If we accept a Jahn–Teller splitting of 0.40 eV in the  $\pi_2$ ,  $\pi_3$  bands, then the lowest energy ionization in cyanuric fluoride which is not already preempted as a  $\pi$  ionization is that at 15.4–15.5 eV. Taking this as the upper lone-pair ionization (e') leads to a tremendous perfluoro shift of almost 5 eV. Application of a shift of this size to the  $a_1'$  lone-pair ionization at 13.25 eV in *s*-triazine places it at 17.9 eV in the fluoride. A  $\sigma$  perfluoro shift of 5 eV in the *s*-triazine–cyanuric fluoride systems is twice as large as that observed for the lone pair in the pyridine–pentafluoropyridine system and

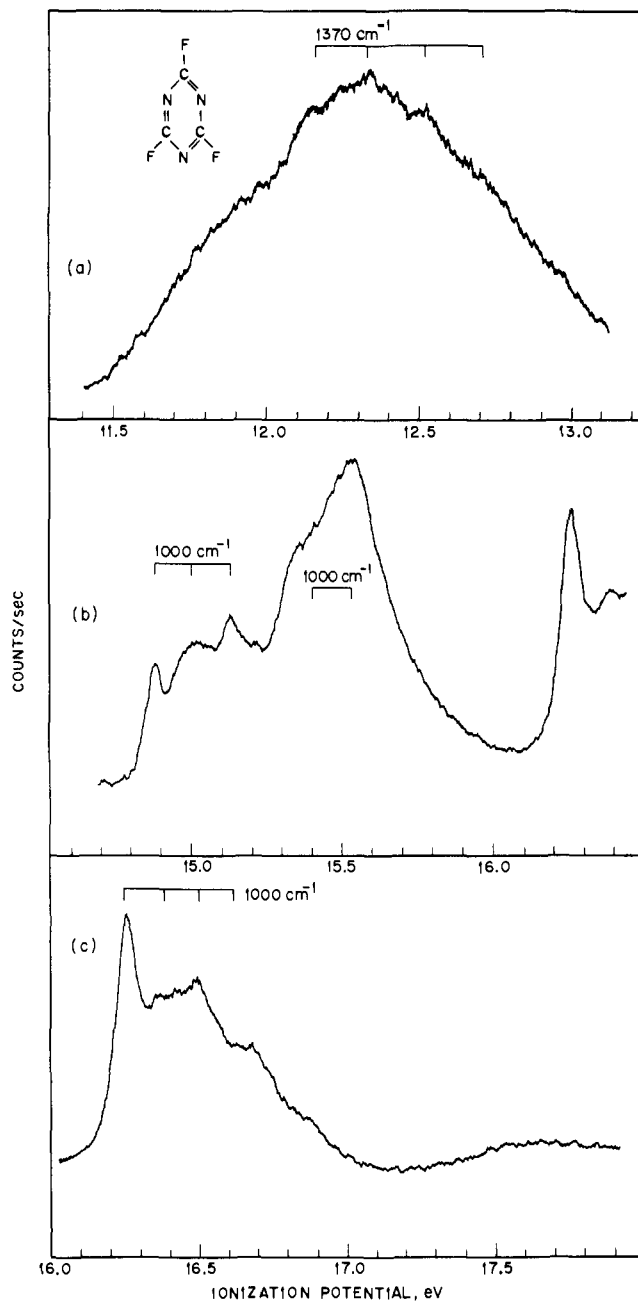


Figure 6. Details of the vibronic structure in the bands of cyanuric fluoride.

offers a good subject for future theoretical calculations. On the other hand, a more reasonable perfluoro  $\sigma$  shift of about 2 eV results if it is assumed that the  $n(e')$  orbital of *s*-triazine is shifted to become one of the two components in the 12-eV region of cyanuric fluoride, with  $n(a_1')$  similarly shifted to the 15.0–15.5-eV region. The latter explanation, proposed to us by S. D. Worley, is more likely the correct one. The stabilization of the lone-pair electrons by several electron volts in cyanuric fluoride is undoubtedly the reason behind the marked lack of basicity in this compound.<sup>28</sup>

In *s*-triazine, the relative intensities of the bands in the He(I) spectrum are unchanged in the He(II) spectrum, whereas for cyanuric fluoride, the features at 16–17 eV are considerably enhanced in the He(II) spectrum.

(28) J. E. Griffiths, personal communication.

**Borazine-*B*-Trifluoroborazine.** Aside from the interesting question of the aromaticity of borazine, its electronic structure is of general interest, particularly as regards its photoelectron spectrum. Recent semiempirical calculations assign the uppermost MO of borazine as a  $\sigma$  MO<sup>29,30</sup> rather than as  $\pi$  as in benzene. Further, referring again to benzene, one would like to know where the higher  $\sigma$  MO's of borazine stand with respect to the  $\pi_2$ ,  $\pi_3$  degenerate pair and the  $\pi_1$  nondegenerate MO. Fortunately, the high-resolution photoelectron spectrum of borazine and its *B*-trifluoro derivative have been reported by Lloyd and Lynaugh,<sup>31</sup> Table IV, and we shall interpret their data using the perfluoro effect. These spectra are nicely complemented by the recent *ab initio* borazine calculations of Peyerimhoff and Buenker.<sup>15</sup>

Comparison of the spectra in question shows immediately that the slightly split first band of borazine (10.14, 10.50 eV) is only shifted to 10.79 eV in the *B*-trifluoride, so this must be the ionization from the  $\pi_2$ ,  $\pi_3$  pair. It is interesting that the borazine  $\pi_2$ ,  $\pi_3$  split (0.36 eV) is very close to those observed for *s*-triazine and cyanuric fluoride (0.4 eV); an incipient splitting is also apparent in the  $\pi_2$ ,  $\pi_3$  bands of *B*-trifluoroborazine. The corresponding  $\pi_1$  ionizations in borazine and *B*-trifluoroborazine should also be within 0.5 eV of each other, and most likely 2.5–3 eV removed from the  $\pi_2$ ,  $\pi_3$  ionizations. These constraints lead to the assignments of the 12.83- (borazine) and 12.98-eV (*B*-trifluoroborazine) bands to ionization from the  $\pi_1$  MO's. Though Lloyd and Lynaugh agree that the first ionization in each molecule is from the  $\pi_3$ ,  $\pi_2$  MO's, they assign  $\pi_1$  in borazine as the 12.06-eV band based on an argument which assigns the benzene spectrum as  $\pi_2$ ,  $\pi_3$ ,  $\pi_1$ ,  $\sigma$ , whereas we deduce the reverse ordering for  $\pi_1$  and  $\sigma$  in benzene. The band or bands in the 11–12.5-eV region of borazine appear in the trifluoride at 13.5–14.5 eV, giving a  $\sigma$  shift of only 2 eV. While this is sufficiently large to show the  $\sigma$  symmetry of the ionizing MO, the size of the shift is much smaller than that proposed for the  $\sigma$  MO's in the *s*-triazine-cyanuric fluoride pair, according to the scheme in which there is a large Jahn-Teller splitting of the degenerate  $\pi$  MO's. The *ab initio* borazine calculation<sup>15</sup> is not in quantitative agreement with the observed vertical ionization potentials, but does concur with the  $\pi_3$ ,  $\pi_2$ ,  $\sigma$ ,  $\pi_1$  ordering dictated by the perfluoro effect. However, in the trifluoride,  $\sigma$  and  $\pi_1$  cross over, resulting in the  $\pi_3$ ,  $\pi_2$ ,  $\pi_1$ ,  $\sigma$  ordering as in hexafluorobenzene, pentafluoropyridine, and cyanuric fluoride.

***p*-Benzoquinone-Tetrafluoro-*p*-benzoquinone.** Turner, *et al.*,<sup>5</sup> have published without comment the photoelectron spectra of *p*-benzoquinone and its perfluoro partner, tetrafluoro-*p*-benzoquinone. In *p*-benzoquinone, there will be two oxygen lone-pair ionizations and two or three  $\pi$ -electron ionizations in the lower energy region, and our hope is to sort them out using the perfluoro effect. We have redetermined these spectra, and they are shown in Figure 7. Note that the band at 12.62 eV in Turner's spectrum of the tetrafluoro derivative is due to water.

(29) P. M. Kusnesov and D. F. Shriver, *J. Amer. Chem. Soc.*, **90**, 1683 (1968).

(30) D. W. Davies, *Trans. Faraday Soc.*, **64**, 2881 (1968).

(31) D. R. Lloyd and N. Lynaugh, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 97 (1970).

Table IV. Ionization Potentials in the Borazine-*B*-Trifluoroborazine Pair<sup>a</sup>

Borazine			<i>B</i> -Trifluoroborazine		
Adiabatic	Vertical	Vibration	Adiabatic	Vertical	Vibration
9.88	10.14	700 ( $\nu_4'$ )	10.46	10.79	1050 ( $\nu_2'$ )
	10.50		12.85	12.98	1500 ( $\nu_2'$ ), 750 ( $\nu_3'$ )
11.11	11.42		13.35	13.53	
	11.73		14.05	14.29	1200 ( $\nu_2'$ )
11.99	12.06		15.42	15.85	
12.60	12.83		16.11	16.20	
13.73	13.84	1900 ( $\nu_2'$ ), 2400 ( $\nu_1'$ )	16.69	16.87	
	14.76		17.67	17.73	
17.10	17.47				
	18.18				

<sup>a</sup> Taken from ref 31.

Our interpretation of these spectra as per the dictates of the perfluoro effect is the following. The band at 13.43 eV in *p*-benzoquinone has clearly suffered a large shift to higher energy in the perfluoro derivative, Figure 7, and is thus a  $\sigma$  MO ionization. However, it is too high to be one of the oxygen lone-pair excitations, which are expected in the 10–12-eV region, with a splitting of about 1 eV.<sup>32</sup> Thus, in the 10–12-eV region of *p*-benzoquinone, there must lie two lone-pair ionizations and one or more (most likely two)  $\pi$  ionizations. Tentatively, we would place these at 10.11, 10.41, 11.06, and 11.5 eV (*cf.* Figure 9.15 in ref 5). In support of this interpretation, Stevenson<sup>33</sup> has calculated the electronic structure of *p*-benzoquinone using the CNDO method and finds the two lone pairs ( $b_{2g}$  and  $b_{1u}$ ) and two  $\pi$  orbitals ( $b_{2u}$  and  $b_{3g}$ ) in the 9.9–11.0-eV region, with the next level coming at about 14 eV. Swenson and Hoffmann<sup>32</sup> have performed extended Hückel and CNDO/2 semiempirical calculations on the lone pair-lone pair interaction in *p*-benzoquinone and find that the two theories place the symmetric combination of lone pairs lower, with predicted splits of 0.47 and 1.92 eV. The splitting between lone pairs is explained by them as due to the delocalization of the lone pairs over the  $\sigma$  framework of the ring (through-bond interaction). Despite this delocalization, the transitions are very vertical in *p*-benzoquinone, and despite the fluorine atoms, they are still rather vertical in the tetrafluoro derivative. This latter observation is surprising, since it was found that in the nonaromatic compounds, the perfluoro partners had strongly nonvertical transitions, even if the corresponding bands in the perhydro compound were very vertical.

The ordering of the lower four bands in *p*-benzoquinone of course is of interest to us, but they are just too close together for the perfluoro effect to give an unambiguous answer; the situation is much like that of the first two bands of pyridine. If we accept the premise that there will be no diminution of an ionization potential on perfluorination, then the 11.5-eV band of *p*-benzoquinone must suffer a shift to 15 eV or beyond in tetrafluoro-*p*-benzoquinone and therefore is a lone-pair ionization. Tentatively, we place the  $n_u$  ionization at 10.11 eV in *p*-benzoquinone (giving an  $n_u/n_g$  split of 1.4 eV) and at 15.01 eV in the tetrafluoro compound. The two  $\pi$  MO's at 10.41 and 11.06 eV in the perhydro compound are then shifted by a few tenths of an

electron volt to 10.72 and 11.18 eV in the perfluoro compound.

The assignments for the lower bands of *p*-benzoquinone are little more than guesses. Their value is in providing an example of how the perfluoro effect obvi-

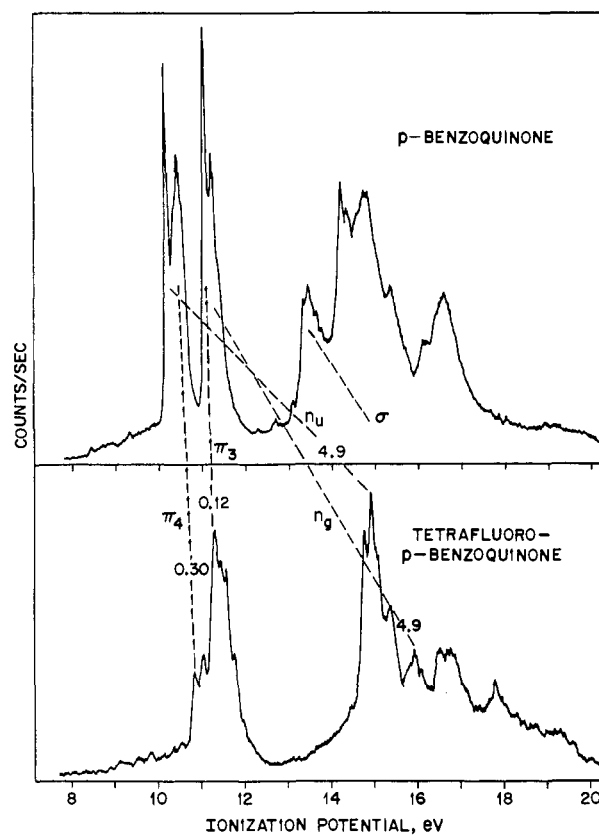


Figure 7. Very tentative correlation of the photoelectron bands of *p*-benzoquinone (upper) and tetrafluoro-*p*-benzoquinone (lower).

ously can be operating in a pair of molecules, and yet the assignments remain ambiguous because of the closeness of  $\pi$  and  $\sigma$  transitions in the perhydro compound. Quite possibly, the photoelectron study of the various alkyl derivatives of *p*-benzoquinone would show the true number of bands in the low-energy region and their assignment, as was the case with pyridine.

**Naphthalene-Octafluoronaphthalene.** In this molecular pair, we again face the recurrent problem: following the first one or two  $\pi$  ionizations, are the following ones  $\pi$  or  $\sigma$ ? According to the *ab initio*

(32) J. R. Swenson and R. Hoffmann, *Helv. Chim. Acta*, **53**, 2331 (1970).

(33) P. Stevenson, private communication.



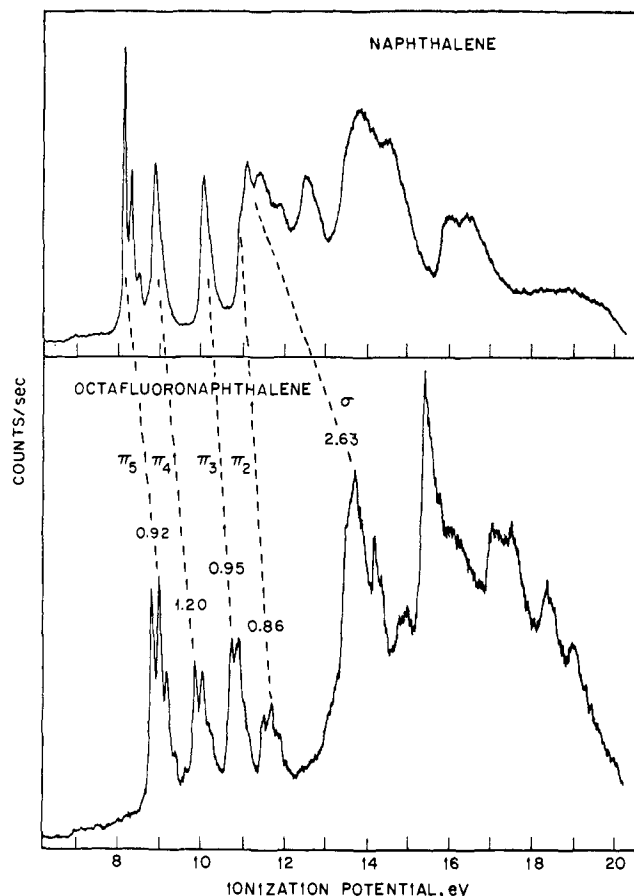


Figure 8. Correlation of the photoelectron bands of naphthalene (upper) and octafluoronaphthalene (lower).

GTO calculation of Buenker and Peyerimhoff,<sup>34</sup> the first four ionization potentials in naphthalene are  $\pi$ , followed by three  $\sigma$  MO's, and then another  $\pi$  MO. Using a semiempirical theory, Eland and Danby calculated  $\pi$ -MO energies and found the first four to agree in energy with the first four transitions observed by them in the photoelectron spectrum.<sup>35</sup> In a similar calculation, but which includes  $\sigma$  MO's as well, Dewar and Worley<sup>36</sup> found the five lowest MO's to be  $\pi$  and the sixth was  $\sigma$ . Our assignments, as derived from the perfluoro shifts, are in agreement with the first four levels being  $\pi$  MO's, but from that point it appears that the  $\sigma$ -MO manifold intrudes.

It is clear from the photoelectron spectra of naphthalene and octafluoronaphthalene, Figure 8, that the  $\sigma$  MO's in the latter have been strongly shifted compared to those of naphthalene, leaving the first four ionizations exposed. These  $\pi$  ionizations, which come at 9.05, 10.08, 10.96, and 11.76 eV in the octafluoro compound, have their counterparts in naphthalene at 8.13 ( $1a_u$ ), 8.88 ( $2b_{1u}$ ), 10.01 ( $1b_{3g}$ ), and 10.90 ( $1b_{2g}$ ) (Table V). The  $\pi$  shifts in the naphthalene-octafluoronaphthalene pair are seen to be about 1 eV, somewhat large for a  $\pi$  shift, but still acceptable. The fifth ionization potential of naphthalene comes at 11.08 eV, and its partner appears at 13.71 eV, or higher, in octafluoronaphthalene. The 2.63-eV shift of this band indicates that a  $\sigma$  MO is involved, as

(34) R. J. Buenker and S. D. Peyerimhoff, *Chem. Phys. Lett.*, **3**, 37 (1969).

(35) H. J. D. Eland and C. J. Danby, *Z. Naturforsch. A*, **23**, 355 (1968).

(36) M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, **50**, 654 (1969).

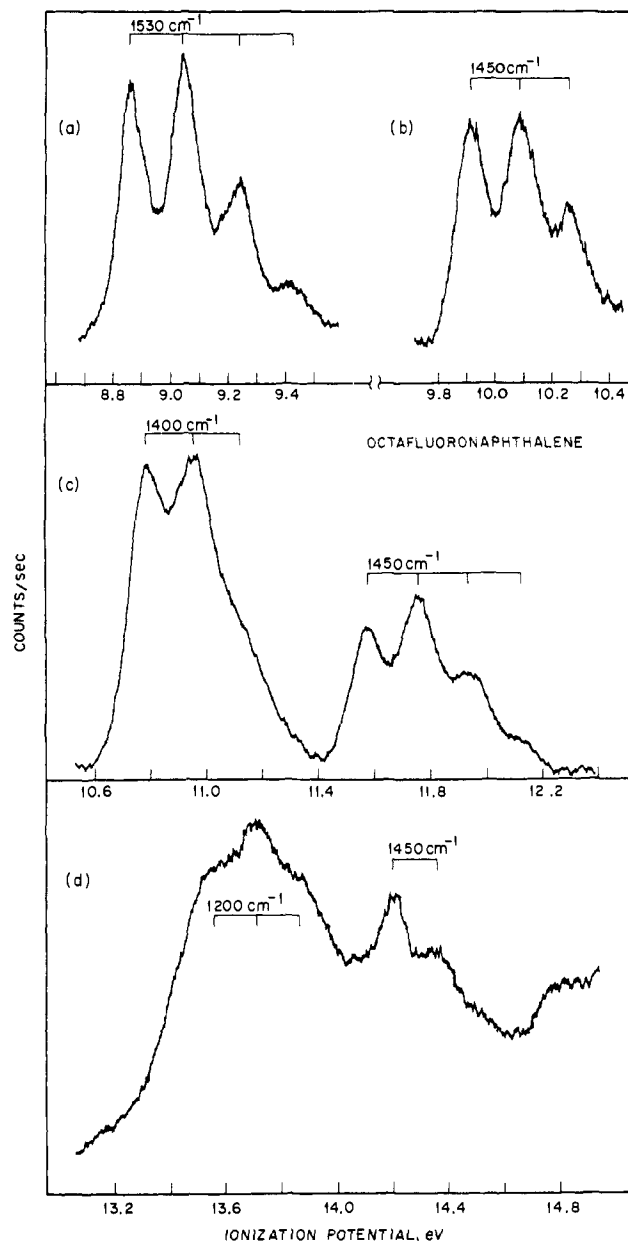


Figure 9. Details of the vibronic structure in the bands of octafluoronaphthalene.

predicted by the GTO calculation ( $9a_g$ ). The analysis cannot be continued beyond this point, since the fluorine lone-pair ionizations enter the picture at about 14–15 eV and hopelessly complicate the interpretations. The vibrational intervals of 1200–1550  $\text{cm}^{-1}$  in the octafluoronaphthalene transitions, Figure 9, could be either ring stretching and/or C–F stretching motions. The 1450- $\text{cm}^{-1}$  interval also appears in the first band of naphthalene itself.<sup>5</sup>

Once again, the relative intensities of the hydrocarbon bands are unaffected by the excitation energy, but a significant change is observed in the perfluoro derivative. In this case, the 15.4-eV band of octafluoronaphthalene is relatively very strong in the He(I) spectrum but has lost about 50% of its intensity under He(II) excitation. Actually, in our spectra we are monitoring the differential cross sections at  $90^\circ$ , so that a decreasing or increasing signal under He(II) excitation is consistent

Table V. Ionization Potentials in the Naphthalene–Octafluoronaphthalene Pair

Naphthalene			Octafluoronaphthalene		
Adiabatic	Vertical	Vibration	Adiabatic	Vertical	Vibration
8.13 (3)	8.13 (3)	1450 ( $\nu_3'$ )	8.85 (3)	9.05 (3)	1530
ca. 8.7	8.88 (4)		9.90 (8)	10.08 (5)	1450
10.01 (1)	10.01 (1)	1050, 400 ( $\nu_9'$ )	10.78 (2)	10.96	1400
10.90	10.90		11.57	11.76	1450
	11.08		ca. 13.0	13.71	1200
	11.37		14.20	14.20	1450
	11.89			14.9	
	12.50			15.4	
	13.8			16.1	
	14.5			17.0	
	16.0			17.5	
	16.5			18.3	
	19.0			18.9	
	22.3			20.1	
				ca. 22.2	
				ca. 24.5	

with either a change in the angular distribution of photoelectrons or a change in the total cross sections.

### Discussion

It is clear from the few examples given here that the general rules governing the perfluoro shifts of  $\pi$  and  $\sigma$  MO's in nonaromatic molecules<sup>1</sup> can be applied equally to aromatics, though the  $\pi$  shift is generally larger in this class of compounds. Moreover, simple comparison of the photoelectron spectra of a perhydro–perfluoro pair allows one to readily identify  $\pi$  and  $\sigma$  ionizations up to about 15 eV, at which point the spectra are swamped by fluorine atom ionizations. The perfluoro effect should be of special value in the photoelectron study of aza- and polyazaaromatics, in which the ionization potentials of the  $\pi$  MO's and the heteroatom lone pairs are intimately tangled,<sup>18,23,37</sup> and in the larger

(37) A. J. Yencha and M. A. El Sayed, *J. Chem. Phys.*, **48**, 3469 (1968).

aromatic hydrocarbons, such as azulene, in which the  $\pi$  and  $\sigma$  MO manifolds are interleaved. A second possible use centers about the fact that the  $\pi$  levels of an aromatic do not shift appreciably on perfluorination if the system is planar. Thus, the comparison of the photoelectron spectra of an aromatic hydrocarbon and its perfluoro derivative can be used to show whether the perfluorinated compound is planar or not. Conversely, we conclude that *B*-trifluoroborazine and cyanuric fluoride are planar molecules in the gas phase, since their photoelectron spectra behave in a regular manner when compared with those of borazine and *s*-triazine.

**Acknowledgment.** The highly purified sample of cyanuric fluoride was prepared by Dr. J. E. Griffiths, and we acknowledge with thanks several conversations with him and with G. Taylor, S. D. Worley, and P. Stevenson.