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An Overlapping Spheres Multiple Scattering Xα Study of the Perfluoro Effect on the Ionisation Potentials and Electron Transmission Spectra of Fluorosubstituted Benzenes

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The overlapping spheres multiple scattering Xα method is used to investigate the nature of the »perfluoro effect« through calculations on the ionisation potentials (IPs), electron affinities (EAs), and elastic cross sections for electron scattering of benzene, para-difluorobenzene, 1,3,5-trifluorobenzene, 1,2,4,5-tetrafluorobenzene and hexafluorobenzene (HXFB). The results of the IP calculations agree with experiment and, for the most part, with HAM/3 calculations but they differ considerably from assignments made with the aid of Hartree-Fock minimal basis set calculations. The calculated derivative curves for electron-molecule scattering agree with the experimentally determined ones, but the detailed interpretation of the elastic cross sections differs considerably from those given previously. In previous work, all the resonances have been interpreted in terms of the unoccupied valence orbitals but in this work the second strong resonance, seen in all the fluorinated benzenes except HXFB, is assigned to a temporary negative ion state formed by electron capture in a $d\pi$ type diffuse Rydberg orbital. In HXFB there is only one strong resonance and this also is assigned to electron capture in a $d\pi$ type orbital. HXFB is the only one of the series for which an experimental value for the bound EA is known (1.8 eV). The theoretical value (1.7 eV) is in good aggrement.

INTRODUCTION

There have been many studies on the nature of the occupied energy levels of molecules both experimentally, through the use of photoelectron spectroscopy (PES) and theoretically.[1,2] By contrast there has been relatively little work done on the characterization either theoretically or experimentally of unoccupied orbitals.[3] In the last few years a number of experimental techniques such as electron transmission spectroscopy (ETS)[3–6] and negative ion photoelectron spectroscopy have been developed,[7,8] and experimental information on electron affinities (EAs) of molecules has begun to become available.[7,8] In order to exploit this information to the fullest, it is necessary to have a theoretical method capable of reliably interpreting the experimental EAs and ETS in terms of molecular structure. There have been many theoretical models proposed for this purpose,[9–12] and these have met with considerable success for atoms and for small diatomic molecules such as hydrogen, nitrogen and hydrogen chloride. However, because of the diffuse nature of negative ions and the importance of electron correlation,[11] traditional quantum mechanical methods based on the Hartree-Fock formalism have had little success for nonlinear polyatomic molecules containing more than one heavy atom, either for the calculation of bound EA's (although the calculation of the EA of the NO_2 radical[12] is a notable exception to this) or unbound EAs (as measured by ETS). Furthermore, attempts to calculate the actual elastic cross sections for electron scattering using Hartree-Fock methods have not as yet progressed beyond one center approaches which limit their application to atoms, to diatomic molecules such as hydrogen, nitrogen, and hydrogen chloride,[9,10] or to polyatomic molecules such as hydrides (methane, ammonia, and water) for which one center expansions are known to be adequate.[13]

By contrast however, the use of local density functional theory[14] in the form proposed by Slater and Johnson,[15–18] known as the multiple scattering $X\alpha$ (MS$X\alpha$) method has been found to be of very great utility, not only for the calculation of ionisation potentials (IPs)[17,18] but also for the calculation of bound EAs for a wide range of polyatomic molecules[18,19] and for a number of continuum properties including the calculation of elastic electron scattering cross sections.[19–21] We present in this paper a systematic attempt, using our particular version of the multiple scattering $X\alpha$ method which uses overlapping spheres (OSMS$X\alpha$ method), to investigate the nature of all the energy levels in benzene and some of it's fluoroderivatives, for which there are experimental data on both the IPs[22] and ETS,[23] with the aim of more thoroughly understanding the well known »perfluoro effect«.[1,24] Whereas there have been many studies on this effect,[1,3] they have been almost entirely confined to the occupied energy levels of the molecules and even then the interpretation of the experimental results in terms of molecular structure is still a matter of great controversy.[22–28] The only experimental studies of the »perfluoro effect« on unoccupied energy levels are two ETS studies,[23,28] one on substituted benzenes[23] and one on substituted ethylenes.[28] Our OSMS$X\alpha$ method was successful in interpreting the ETS spectra of the fluoroethylenes,[29] and here we show the method also gives a satisfactory interpretation of the ETS of the fluorobenzenes although this interpretation is very different than those given previosuly.[23,30]

METHOD

The bound-state MS$X\alpha$ method has been described in detail elsewhere.[15–18] The electrons of a molecule are assumed to move in a spherically averaged molecular field which is divided up into three regions. Region I consists of spheres of radius R_I around each atom. Region III is that region outside a radius R_{III} (the outer sphere radius) which encompasses the whole molecule. (Note this region was not present in the original MS$X\alpha$ method but is needed for many applications.) Region II is a region of constant potential between regions I and III. In the original method,[15,16] the atomic spheres were allowed only to touch (muffin-tin approximation) and the outer sphere was drawn tangentially to the atomic spheres. It is now well known[17,18] that the muffin-tin approximation results in too much electron transfer from the atomic spheres (region I) to the constant potential region (region II). However, this deficiency can be removed[17,18] if the atomic spheres are allowed to overlap, *i. e.*, the OSMS$X\alpha$ method.

In our previous work[31] we proposed a method of choosing the amount of overlap by examining the radial charge distributions calculated for the atoms.

The radii of the atomic spheres used in this paper for hydrogen, carbon, and fluorine are those obtained by this method and used in our previous work.[19,21,29,31] They are $R_H = 1.109$ a. u., $R_C = 1.627$ a. u., $R_F = 1.319$ a. u. The same value of the Slater exchange[15] parameter ($\alpha = 0.75$) was used for all three regions. The use of these values makes the method completely free of any type of parameterization which is dependent on other methods of calculation or on any experimental data. Basis sets of l values up to 3 and 5 for regions I and III were used in the bound state calculations, and l values up to 5 and 7 for the respective regions were employed in the continuum calculations for electron scattering. In a test case for 1,3,5-trifluorobenzene, increasing the l values to 6 and 8 respectively was found not to change the results significantly over the energy range 0 to 6 eV. The IPs and bound EAs were obtained using Slater's half-occupation transition state method.[15] The method of calculating the elastic cross sections (Table III and Figures 2 and 3) are the same as described previously,[19,21] *i. e.* method II of reference 19. This method, the energy dependent Hara free-electron gas approximation for exchange between the target molecule and the incoming electron, was employed for all the electron scattering calculations. A somewhat similar parameter free method has recently been proposed by O'Connell and Lane and applied to rare gas atoms.[32] Their method differs mainly from the method described here in that they define an explicit correlation potential in the inner target region, and they use the results of bound state Hartree-Fock calculations to calculate the static potential.

Our use of a spherically averaged potential in the outer sphere region III would appear to make the OSMSXα method unsuitable for scattering calculations on molecules whose potentials are strongly anisotropic. However, our previous work on nitrogen indicates this need not be a serious problem.[19] Our OSMSXα calculations for this molecule were not only successful in predicting correctly the position and the elastic total cross section of the low energy $^2\pi_g$ resonance, even though it possesses considerable outer sphere character, but the individual partial wave cross sections for energies up to 50 eV were also found to agree very well with those calculated using the best anisotropic potential available.[19]

IONISATION POTENTIALS

The concept of the »perfluoro effect« was first introduced by Brundle and Robin in 1972.[24] Since then there have been many examples of it's utility in distinguishing ionisation potentials arising from σ type orbitals from their π type counterparts.[21,25,27] However, although the utility of the use of this concept as an empirical tool is unquestioned, the nature of the electronic factors responsible for the unique behavior of fluorine is still a matter of considerable controversy. There have been many discussions of the effect of fluorine substituents on the PES of benzene.[25–27] The early experimental work and it's interpretation has been reviewed by Price *et al.*[26] and by Duke *et al.*[25] The latter authors also used a semiempirical method, the CNDO/S2 method to interpret the resluts. More recently Palmer *et al.*,[27] after reviewing earlier work, presented a set of new assignments for the PES of fluorobenzene (FB), the disubstituted fluorobenzenes (DFB), 1,3,5-trifluorobenzene (TFB), and hexafluorobenzene (HXFB). In making these assignments, they put considerable reliance on the results of minimal basis set Hartree-Fock calculations. In 1981

Bieri *et al.*[22] published the He(II) PES of thirty fluoro-compounds, including all the fluoro-derivatives of benzene, together with assignments based upon the semiempirical HAM/3 method and on an *ab initio* many-body Greens function calculation on para-difluorobenzene (PDFB).[33] The assignments made by the latter authors differed considerably from the ones made by Palmer *et al.*[27] and by Duke *et al.*[25]

Most of the differences between the assignments arise from assigning which ionisations stem from orbitals that are mainly fluorine in character. Previously we have had considerable success in using the OSMSXα method to assign the PES of tetrafluoroethylene[31] and of tetrafluorobenzoquinone (TTFBQ),[31] the latter work being presented in a revised version in the Appendix of the present paper. Here we present the results of a similar study on the interpretation of the PES of PDFB, TFB, 1,2,4,5-tetrafluorobenzene (TTFB), and HXFB. It has often been claimed that the OSMSXα method should not be very good for planar organic molecules because the muffin-tin approximation is particularly bad for this type of molecule. However, the work of Case *et al.*[34] on the application of the method to the calculation of the ionization potentials of benezene (B), and a number of it's nitrogen derivatives, shows that with an appropriate choice of parameters, particularly the size of the atomic spheres, the results are very reasonable. Our results (Table I) confirm this conclusion.

TABLE I

Experimental and Calculated IPs of Fluorobenzenes[a]

PDFB (D_{2h})					TFB (D_{3h})			
	IP/eV					IP/eV		
Orbital[b]	OSMSXα	HAM/3[c]	GF[d]	Exp.[e]	Orbital	OSMSXα	HAM/3	Exp.[e]
2 b_{3g} (πB)	9.27	9.50	9.37	9.33	2 e'' (πB)	9.72	10.08	9.8
1 b_{2g} (πB)	9.56	10.27	10.02	10.0				
4 b_{1g}' (σB)	13.20	12.49	12.77	12.5				
2 b_{1u} (πB)	11.95	11.93	12.86	12.5	2 a_2'' (πB)	12.46	11.98	12.5
5 b_{3u} (nF)	13.16	13.20	14.12	13.6	9 e' (nF)	13.85	13.73	13.6
8 a_g (σB)	14.48	14.34	14.38	14.3	2 a'_2 (nF)	14.16	13.35	14.0
4 b_{3u} (σB)	15.12	15.07	15.39	15.1				
3 b_{1g} (nF)	15.37	15.00	15.96	15.4				
7 b_{2u} (σB)	15.61	15.66	15.81	15.7				
					8 e' (σB)	15.51	15.25	15.4
1 b_{3g} (πF)	15.87	15.76	16.81	16.0	1 e'' (πF)	15.83	16.03	15.8
1 b_{1u} (πF)	16.58	15.95	16.91	16.8	1 a_2'' (πF)	16.33	16.49	16.4
					7 a_1' (σB)	17.19	16.82	17.0
3 b_{3u} (σB)	17.23	16.45	17.96	17.2	7 e' (σB)	17.57	17.10	17.4
6 b_{2u} (σB)	18.68	18.08	18.20	18.0	1 a_2'(σB)	18.48	17.30	18.3
7 a_g (σB)	18.09	17.30	18.73	18.5	6 a_1' (σB)	19.60	18.88	19.5
2 b_{1g} (σB)	20.34	19.58	21.48	20.0	6 e' (σB)	21.18	20.16	21.0
6 a_g (σB)	20.59	19.59	22.13	20.6				
2 b_{3u} (σB)	23.39	23.70	26.70	24.0	5 e' (σB)	24.30	24.00	24.2
5 b_{2u} (σB)	23.68	23.49	26.55	24.0				
5 a_g (σB)	26.16	27.28	30.43	26.2	5 a_1' (σB)	26.58	27.68	26.4

TTFB (D_{2h})				HXFB (D_{6h})			
	IP/eV				IP/eV		
Orbital	OSMSXα	HAM/3	Exp.	Orbital	OSMSXα	HAM/3	Exp.
$2\,b_{2g}$ (πB)	9.77	9.92	9.5	$2\,e_{1g}$ (πB)	11.27	10.68	10.12
$2\,b_{3g}$ (πB)	10.57	10.59	10.3				
$2\,b_{1u}$ (πB)	12.76	12.07	12.5	$2\,a_{2u}$ (πB)	13.09	12.30	12.77
$9\,a_{g}$ (nF)	13.51	13.61	13.6	$2\,b_{2u}$ (nF)	14.39	13.72	14.02
$7\,b_{3u}$ (nF)	13.81	13.48	13.8	$6\,e_{2g}$ (nF)	14.84	14.74	14.77
$6\,b_{1g}$ (nF)	14.52	14.63	14.7	$1\,a_{2g}$ (nF)	15.90	15.61	15.82
$8\,b_{2u}$ (nF)	14.77	15.27†	14.7	$6\,e_{1u}$ (nF)	16.05	15.81	16.0
$1\,a_{u}$ (πF)	15.55	15.67	15.5	$1\,b_{2g}$(πF)	16.39	15.88	16.4
$1\,b_{3g}$ (πF)	15.59	15.88	15.8	$1\,e_{2u}$ (πF)	16.54	16.16	16.6
$7\,b_{2u}$ (σB)	15.76	16.02	16.0				
$8\,a_{g}$ (σB)	15.90	16.11	16.2				
$1\,b_{2g}$ (πF)	16.48	16.66	16.4	$1\,e_{1g}$ (πF)	17.03	17.23†	16.9
$1\,b_{1u}$ (πF)	16.70	17.08†	16.6	$1\,a_{2u}$ (πF)	17.52	18.21†	17.6
$5\,b_{1g}$ (σB)	17.31	16.66	17.3	$5\,e_{2g}$ (σB)	18.34	18.18	18.3
$6\,b_{3u}$ (σB)	18.22	17.71	18.1	$5\,e_{1u}$ (σB)	18.90	18.48	18.7
$5\,b_{3u}$ (σB)	19.04	18.11	18.9	$1\,b_{2u}$ (σB)	20.66	19.39	20.3
$6\,b_{2u}$ (σB)	19.45	19.12	19.5	$4\,b_{1u}$ (σB)	20.68	20.10	20.3
$7\,a_{g}$ (σB)	19.46	18.41†	19.5	$5\,a_{1g}$ (σB)	20.81	19.18	20.3
$6\,a_{g}$ (σB)	21.02	20.60	21.0	$4\,e_{2g}$ (σB)	22.85	21.45	22.4
$4\,b_{1g}$ (σB)	21.45	20.15	21.6				
$5\,b_{2u}$ (σB)	24.38	24.43	24.8	$4\,e_{1u}$ (σB)	25.84	25.32	25.5
$4\,b_{3u}$ (σB)	24.60	24.37	24.8				
$5\,a_{g}$ (σB)	26.38	28.11	26.3	$4\,a_{1g}$ (σB)	27.26	29.04	27.3

[a] The assignments given here for IPs greater than 20 eV which are based on one electron models are not strictly valid because it is well known, *e.g.* see L. S. Cederbaum and W. Domcke, *Adv. Chem. Phys.* **36** (1977) 205, that many body effects can cause splitting of the ionization peaks of inner valence electrons into a multitude of components. Usually, however, one or two of these have a much greater intensity than the other lines so that the one electron model assignments are still approximately correct as can be seen by the results quoted in Ref. 22.

[b] The designation B or F in parentheses classifies an orbital according to primarily either benzene or fluorine 2*p* origin; both classifications are based upon OSMSXα population analyses. The notation *n* or π for F type orbitals is intended only to label these respectively as to in-plane π or out-of-plane π. It is not meant to imply that there is no C—F mixing in such orbitals; see text for details.

[c] HAM/3 results are taken from Ref. 22. In D_{2h} symmetry, the group theory representations given here result from choosing the *Z* coordinate out-of-plane and *Y* along the C_2 axis. To obtain agreement in Ref. 22 with our choice of axes in D_{2h}, one must interchange the numbers 1 and 2 for any representation in which these occur.

[d] The Green's function (GF) calculations are from Refs. 22 and 32. For IPs greater than 20 eV, numbers quoted are those of greatest relative intensity.

[e] References 22 and 26.

† The dagger denotes each of the five instances where the HAM/3 assignments to experimental band envelopes differ somewhat from those presented here. For these actual HAM/3 assignments see Ref. 22.

The IP results of our OSMSXα method are compared with experiment and with the HAM/3 results[22] in Table I. In general the agreement, both with experiment and with the HAM/3 results, is surprisingly good especially when one considers how different are the premises upon which both methods are based. The HAM/3 method contains an inordinate amount of parameterization carefully chosen to reproduce the observed PES spectra of a great number of molecules. There is also built into it the distillation of many years experience, by Lindholm and his collaborators, on the interpretation of experimental PES. By contrast the OSMSXα method, as used in this study, contains no molecular parameters adjusted to fit experimental data.

The major difference between the assignments given in Table I and the assignments of Palmer *et al.*[27] arises largely from the method used in the latter study for assigning the peaks caused by the ionisation of the fluorine lone pair electrons (labelled nF and πF in Table I). Palmer *et al.*,[27] in making their assignments, rely considerably on the results of Hartree-Fock minimal basis set orbital energy calculations. However, since this type of calculation always gives orbital energies which are much deeper by a variable amount than the observed IPs, it is sometimes difficult to make a one-to-one correspondence between theory and experiment. Palmer *et al.* also assumed that in FB, the IP due to the F_{2p} orbital occurs at 16.84 eV*. They were then reluctant to accept an IP value less than this for a fluorine orbital in PDFB although a value of 16.8 eV was indicated by the Green's function[33] calculation on this molecule. This led them to assign the two πF IPs in this molecule to a peak at 17.3 eV. On the other hand the HAM/3 method places the πF IP in FB at 16.4 eV, and for PDFB both the HAM/3 and the OSMSXα calculations agree with the Green's function assignment of 16.8 eV for the two πF IPs (Table I). The differences between the HAM/3 and OSMSXα assignments and those made by Palmer *et al.*[27] become even more obvious in TFB and HXFB. In TFB Palmer *et al.* place one πF ionisation under the broad band between 17—18 eV (for the 1 e'' orbital). They then assign the remaining πF ionisation (1 a_2'') to the peak at 18.5 eV, which they also assign to the 7 a_1'orbital. We prefer to assign the πF IPs to much lower values (at 15.8 and 16.4 eV respectively). In HXFB we assign the πF IPs to peaks in the 16.5—17.7 eV region, whereas Palmer *et al.* assign them to peaks in the 17.5—18.8 eV region.

The net result of these assignment differences is that for some of the bands deeper than 16 eV, we place a different number of IPs under a particular PES band than do Palmer *et al.*, usually less at deeper energies. For example, in TFB Palmer *et al.* place four ionisations (7 e' and 1 e'') under the peak observed in the 17.2—18.0 eV region whereas we (Table I) only place two ionisations (7 e') under this peak. Another major difference between all three methods under discussion is the number of IPs deemed responsible for the peak observed in the 18.0—19.0 eV region in HXFB. Palmer *et al.* place six ionisations (corresponding to four non-degenerate orbitals) under this peak. Bieri *et al.*, using the HAM/3 method, place five IPs (5 e_{1u}, 5 e_{2g}, 1 a_{2u}) under this peak, but here using the OSMSXα method, we place only four IPs (5 e_{1u}

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* The published PES spectra[22,26] show a broad band in this region to which several IPs are assigned. It is not clear how Palmer *et al.* arrived at the precise value for this IP.

and 5 e_{2g}) under this peak. These differences suggest that it may be possible to distinguish experimentally between the various assignments. Asbrink *et al.*[33,35,36] have pointed out that, for carefully measured He(II) spectra, the area under an observed PES peak is proportional to the number of ionisations responsible for that peak. Such data is not yet available for the polyfluorobenzenes. However, it is hoped that the results presented here will stimulate research in this area. The required data are available for para-benzoquinone (PBQ) and the perfluorinated tetrafluorobenzoquinone (TTFBQ).[36] In the Appendix to this paper we show that our assignments for PBQ and TTFBQ using the OSMSXα method are in good agreement with the experimental data, especially for areas under those peaks caused by the ionisation of fluorine type orbitals. The success of the OSMSXα method for TTFBQ can be taken as circumstantial evidence that our assignments for the polyfluorobenzenes could be correct also.

The good fit between experimental IPs and the calculated IPs shows that the OSMSXα method is capable of reproducing the observed »perfluoro effect,« at least for this property. The interpretation of the nature of the »perfluoro effect« given by this method is, however, very different from the conventional discussions based on LCAO perturbation theory.[30] There appears to be no direct analogue in the OSMSXα method to the conventional idea of the inductive effect. As can be seen from Table I, the energy levels of molecular orbitals (MOs) labeled B, corresponding to the original benzene types, are certainly shifted to deeper energies across the series of fluorobenzenes, many of the σ MOs by several electron volts. The calculated energy shifts relative to the parent benzene MOs are given in Table II. However, OSMSXα fluorine population analyses (designated %F in Table II) show that there is relatively little correspondence between the induced shifts and the mixing in of fluorine density in the individual orbitals. For example, in TFB, the first five σ benzene-like IPs of this system are *all* moved to higher energies by at least 3.5 eV (Table II, orbitals 3, 4, 6—8). However, in the 1 a_2' orbital (benzene orbital 8) the fluorine 2*p* orbital population is only 0.34 *e* compared to F2*p* orbital populations of 0.87 *e* in each of the 7 e' orbitals (benzene orbitals 6, 7), which are shifted on fluorine substitution by the same amount. In HXFB, where there is much more mixing, the benzene σ type orbitals give rise to IPs in the 18—21 eV region (Table I). These have, except for the 1 b_{2u} orbital, F2*p* orbital populations of between fifty and seventy percent. In the spectra shown in Figure 1, their band structures (Figure 1e) bear little resemblance to the original benzene bands (Figure 1a), but they are easily distinguishable from the orbitals which are primarily fluorine lone pair types since these latter orbitals have a fluorine 2*p* character of more than seventy percent. Indeed, the fluorine π type lone pair orbitals in HXFB have over ninety-five percent F2*p* character, except for the 1 a_{2u} orbital which has only seventy percent F2*p*. In Figure 1 the IPs of the fluorobenzenes are related to the fifteen benzene valence IPs by the same numbers listed in Table II. The vertical lines under the experimentally observed peaks are the assignments made according to the OSMSXα results given in Table I. This figure shows clearly where the IPs from the πF and *n*F type lone pair orbitals arise and also how many orbital ionisations (the vertical lines) are assigned by the OSMSXα method to each band envelope.

TABLE II

Fluorine Induced Shifts of Benzene Ionisation Energies

B (D_{6h})			PDFB (D_{2h})			TFB (D_{3h})			TTFB (D_{2h})			HXFB (D_{6h})		
MO[a] No.	Sym. Assn.	Exp. IP/eV	Sym. Assn.	Exp. Δ^b eV	%[c] F	Sym. Assn.	Exp. Δ eV	% F	Sym. Assn.	Exp. Δ eV	% F	Sym. Assn.	Exp. Δ eV	% F
1	1 e_{ig} (π)	9.24	2 b_{3g} (π)	0.09	14.8	2 e'' (π)	0.56	11.9	2 b_{3g} (π)	1.06	8.9	2 e_{1g} (π)	0.88	21.7
2			1 b_{2g} (π)	0.76	0.0			11.9	2 b_{2g} (π)	0.26	20.6			21.7
3	3 e_{2g} (σ)	11.49	4 b_{1g} (σ)	1.01	14.0	8 e' (σ)	3.91	29.9	5 b_{1g} (σ)	5.81	37.5	5 e_{2g} (σ)	6.81	52.0
4			8 a_g (σ)	2.81	6.8			29.9	8 a_g (σ)	4.71	36.0			52.0
5	1 a_{2u} (π)	12.3	2 b_{1u} (π)	0.20	16.1	2 a_2'' (π)	0.20	24.7	2 b_{1u} (π)	0.20	29.0	2 a_{2u}(π)	0.47	38.9
6	3 e_{1u} (σ)	13.9	4 b_{3u} (σ)	1.20	9.4	7 e' (σ)	3.50	43.3	6 b_{3u} (σ)	4.20	26.9	5 e_{1u} (σ)	4.80	60.2
7			7 b_{2u} (σ)	1.80	0.6			43.3	7 b_{2u} (σ)	2.10	19.2			60.2
8	1 b_{2u} (σ)	14.7	3 b_{3u} (σ)	2.50	21.0	1 a_2' (σ)	3.60	16.8	5 b_{3u} (σ)	4.20	49.6	1 b_{2u} (σ)	5.60	19.4
9	2 b_{1u} (σ)	15.4	6 b_{2u} (σ)	2.60	59.5	7 a_1' (σ)	1.60	0.8	6 b_{2u} (σ)	4.10	66.0	4 b_{1u} (σ)	4.90	67.3
10	3 a_{1g} (σ)	16.84	7 a_g (σ)	1.66	20.2	6 a_1' (σ)	2.66	57.8	7 a_g (σ)	2.66	54.5	5 a_{1g} (σ)	3.46	64.6
11	2 e_{2g} (σ)	19.2	2 b_{1g} (σ)	0.80	4.4	6 e' (σ)	1.80	24.0	4 b_{1g} (σ)	2.40	41.0	4 e_{2g} (σ)	3.20	27.2
12			6 a_g (σ)	1.40	45.6			24.0	6 a_g (σ)	1.80	14.6			27.2
13	2 e_{1u} (σ)	22.6	2 b_{3u} (σ)	1.40	0.5	5 e' (σ)	1.60	8.3	4 b_{3u} (σ)	2.20	13.2	4 e_{1u} (σ)	2.90	12.0
14			5 b_{2u} (σ)	1.40	13.6			8.3	5 b_{2u} (σ)	2.20	6.4			12.0
15	2 a_{1g} (σ)	25.9	5 a_g (σ)	0.30	3.9	5 a_1' (σ)	0.50	4.5	5 a_g (σ)	0.40	5.8	4 a_{1g} (σ)	1.40	7.3

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[a] The benzene (B) molecular orbitals (MOs) are numbered consecutively in this column. These numbers are the same as those in Figure 1 which shows their relationships to the experimental band envelopes.

[b] The shifts (Δ) are defined as the differences between the accepted experimental assignments (columns 2 and 3) for the benzene IPs (ref. 34) and the OSMSXα fluorinated benzene assignments labeled B in Table I.

[c] Percent fluorine character (%F) for each MO is derived from an OSMSXα population analysis which, upon attaining self-consistency, renormalizes the one-electron density in molecular regions II and III to atomic region I. (See text under Method for the definitions of regions I, II and III.)

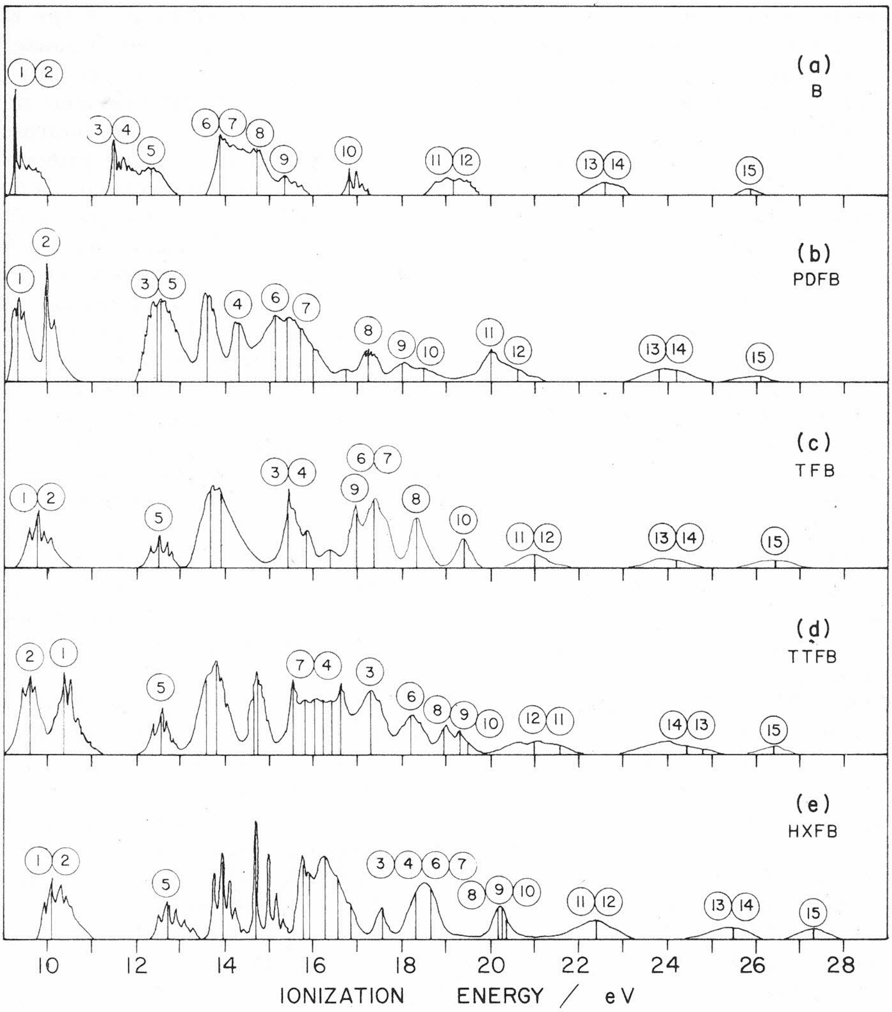

Figure 1. Comparison between experimental band envelopes (ref. 26) and Table I OSMSXα assignments (vertical lines), except for benzene (B) for which the assignments are as in Table II. Circled numbers refer to benzene type IPs in each compound as deduced from the calculations reported in Table I. The actual numbers are from column one of Table II.

THE ELECTRON TRANSMISSION SPECTRA

The ETS of benzene and many of its fluorosubstituted derivatives have been measured by Frazier *et al.*[23] An interpretation of the spectra was given by them only in terms of the unoccupied π^* orbitals of the neutral molecule. Their interpretation has been criticized by Jordan and Burrow[30] who gave an alternative interpretation which, however, was again only in terms of the substituent fluorines perturbing the unoccupied π^* orbitals of the parent benzene. In view of the fact that HXFB is well known[37] to have a positive (bound) EA and that the use of Hartree-Fock virtual orbital energies has difficulty in even accounting for the effect of fluorine substituion in the ETS assignments of fluoroethylenes,[28] whereas the OSMSXα method because of its unique ability of calculating elastic cross sections was able to account for the ETS of both the fluorosubstituted and chlorosubstituted ethylene derivatives,[29] it seemed very desirable to test the method out on the fluorosubstituted benzenes. As discussed below, the method does in fact provide a successful interpretation of the observed spectra, but this interpretation is very different from the previous interpretations because, in order to give a consistent interpretation of the ETS for all the polyfluorobenzene derivatives, it is found necessary to assign some of the resonances, previously assigned to the π^* antibonding valence orbitals, to strong resonances involving temporary electron capture by orbitals which are primarily Rydberg in character, *i. e.*, to orbitals which possess considerable outer sphere character.

The OSMSXα method gives a total cross section profile of benzene which is very similar to that reported by Allan,[5] *i. e.*, it has a very strongly dropping background of nonresonant partial waves, with increasing incident energy, on which are superimposed two π^* resonances, one calculated at 1.05 eV (e_{2u}) with an $l = 3$ barrier and a width (at half-max) of 0.05 ± 0.005 eV, and a much broader one ($l = 4$ barrier) at 4.8 eV (b_{2g}). There is also present, according to the calculations (Table III), a weak and very broad resonance of $d\pi$ (e_{1g}) type which would be hard to discern in the observed ETS curve because of the steeply dropping background. The presence of this Rydberg type resonance can also not be detected in either the theoretical or the experimental derivative spectra (Figure 2a).

The ETS of PDFB (Table III) shows the expected resonance at 4.5 eV, calculated in the b_{3g} channel at 4.7 eV (see Figure 3a), which is undoubtedly due to the third π^* orbital. In the low energy region there are observed apparently two resonances, one at 1.41 eV and one at 0.61 eV. The usual interpretation of these is to ascribe the upper one to a slightly destabilized benzene π^* orbital and the lower one to a strongly stabilized benezene π^* orbital. Unlike LCAO theory however, the OSMSXα method predicts both π^* type resonances to be stabilized relative to benzene and splits them by only 0.3 eV (Table III). The $d\pi$ resonance ($b_{2g} + b_{3g}$), which is very broad and virtually undetectable in benzene, has in PDFB a total channel cross section similar in magnitude to the other π^* resonances (Figure 3a) and should appear at slightly higher energy than the expected π^* type resonances. These predictions, together with the finding by Frazier *et al.*[23] that there is clear evidence for two different overlapping vibrational progressions in the transmission spectra in the 0.3—0.9 eV region (Figure 2b), lead us to suggest the possibility that in PDFB the low energy ETS is made up of two resonances, not one as has been previously claimed,[23] and that the structureless resonance observed inflecting at 1.4 eV is not a π^* resonance but is due to electron capture by a $d\pi$ type Rydberg orbital. The calculations also predict the presence of two strong σ type resonances of b_{2u} and b_{3u} symmetry just above threshold, *i. e.*, between 0.0 and 0.3 eV. These two resonances are, we believe, responsible for the hump seen in both the experimental and theoretical derivative curve in this low energy region (Figure 2b) for PDFB.

The assignments for the resonances observed in TFB have been discussed previously.[19] Additional circumstantial support for the $d\pi$ assignment made in PDFB stems by analogy to this system. In TFB the D_{3h} symmetry allows

TABLE III

Assignments of Resonances Observed in ETS

Target	Symmetry Assignments*		Resonances/eV		Theoretical Cross Sections**		
Molecule	Channel (p)	Type	OSMSXα	Exp.*** (Vert.)	σ_p/Å^2	l of σp/%	σ_T/Å^2
B (D_{6h})	b_{2g}	π^*	4.89	4.80	9.7	99 g	78.6
	e_{1g}	$d\pi$	1.80	—	18.0	98 d	98.1
	e_{2u}	π^*	1.05	1.37	100.0	99 f	222.1
	e_{1u}	$p\sigma$	0.40	—	60.5	99 p	293.3
	a_{2u}	$p\pi$	0.15	—	303.3	100 p	521.8
	a_{1u}	$s\sigma$	0.0	—	300.0	100 s	399.3
PDFB (D_{2h})	$b_{2u}+b_{3u}$	σ^*	6.67	—	32.2	17 p, 67 f	96.2
	b_{3g}	π^*	4.69	4.51	17.8	42 d, 57 g	119.1
	$b_{2g}+b_{3g}$	$d\pi$	1.20	1.41	64.1	99 d	249.7
	b_{1u}	π^*	0.90	0.61	55.1	63 p, 36 f	292.3
	a_u	π^*	0.61	0.61	55.5	99 f	351.8
	$b_{2u}+b_{3u}$	$p\sigma$	0.20	—	469.6	100 p	559.4
TFB (D_{3h})	e'	σ^*	5.65	—	54.1	9 p, 23 d 20 f, 41 g	132.3
	a_2''	π^*	4.23	4.48	15.4	46 p, 45 f, 7 g	138.3
	a_2''	$p, f\pi$	2.25	—	37.6	51 p, 46 f	217.0
	e''	$d\pi$	0.78	0.77	107.7	98 d	326.7
	e'	$p\sigma$	0.0	—	363.0	100 p	389.5
TTFB (D_{2h})	$b_{2u}+b_{3u}$	σ^*	5.51	—	31.6	23 p, 63 f	104.7
	b_{3g}	π^*	4.49	4.51	18.6	48 d, 50 g	122.2
	a_u	$f\pi$	1.23	—	1.8	97 f	274.1
	$b_{2g}+b_{3g}$	$d\pi$	0.95	1.29	91.8	99 d	316.6
	b_{1u}	π^*	0.44	0.50	107.3	95 p	420.0
	$b_{2u}+b_{3u}$	$p\sigma$	0.07	—	1069.8	100 p	1157.4
HXFB (D_{6h})	b_{2g}	π^*	4.63	4.50	1.9	98 g	138.1
	e_{1u}	σ^*	4.55	4.50	39.4	42 p, 52 f	139.2
	e_{1g}	$d\pi$	0.51	0.41	154.2	99 d	382.4

* An asterisk following σ or π denotes a shape resonance due to the formation of a negative ion state (NIS) in which the electron is trapped in a valence type orbital. The absence of the asterisk signifies that the resonance is due to an NIS in which the electron is trapped in a Rydberg diffuse type orbital. Resonance positions are determined by inspecting the variations in channel eigenphase sums as described in Ref. 20.

** σ_p is the cross section of the pth channel responsible for the resonance behaviour. σ_T is the total cross section, that is σ_p plus the sum of all non-resonant channel contributions at the same energy. If the relative difference between these two quantities is large, resonance behaviour may not be discernible in the experimental derivative curve.

*** Reference 23.

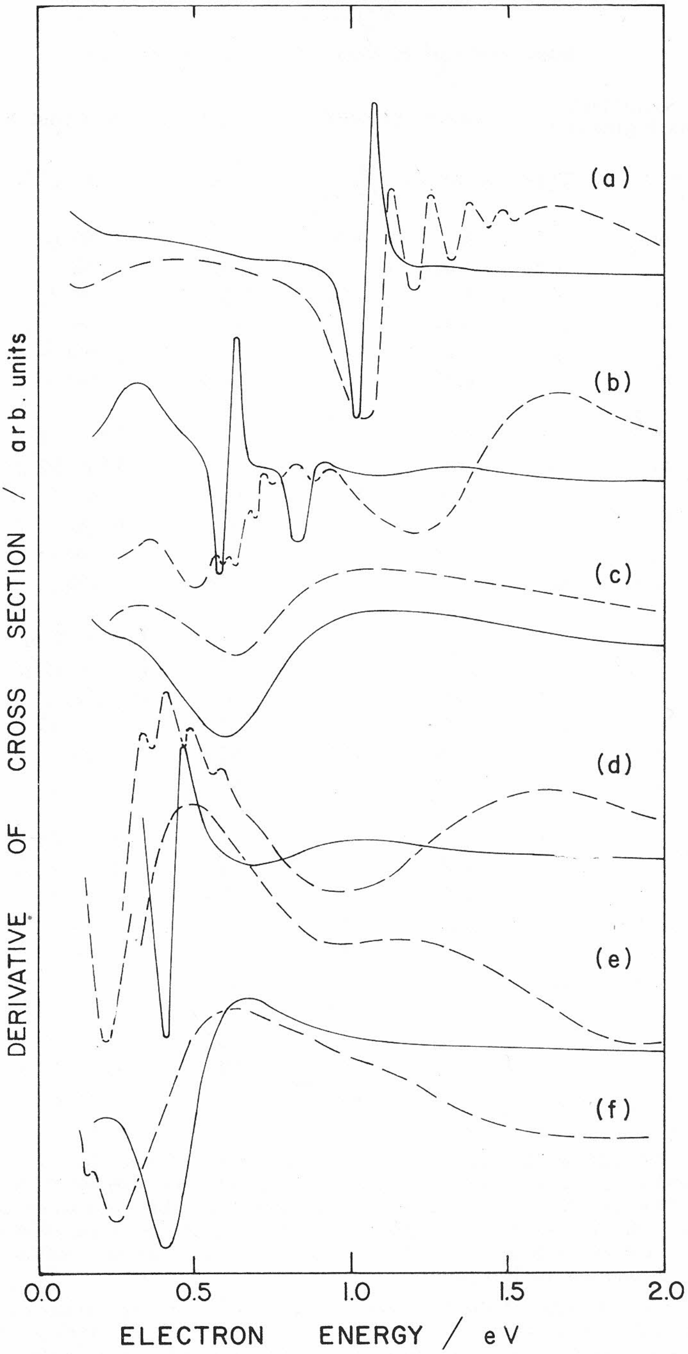

Figure 2. Comparison of theoretical (—) and observed (— —) ETS derivative spectra for benzene and selected fluorobenzenes: (a) B; (b) PDFB; (c) TFB; (d) TTFB; (e) PTFB (experimental only); (f) HXFB. The experimental ETS curves are from Ref. 23.

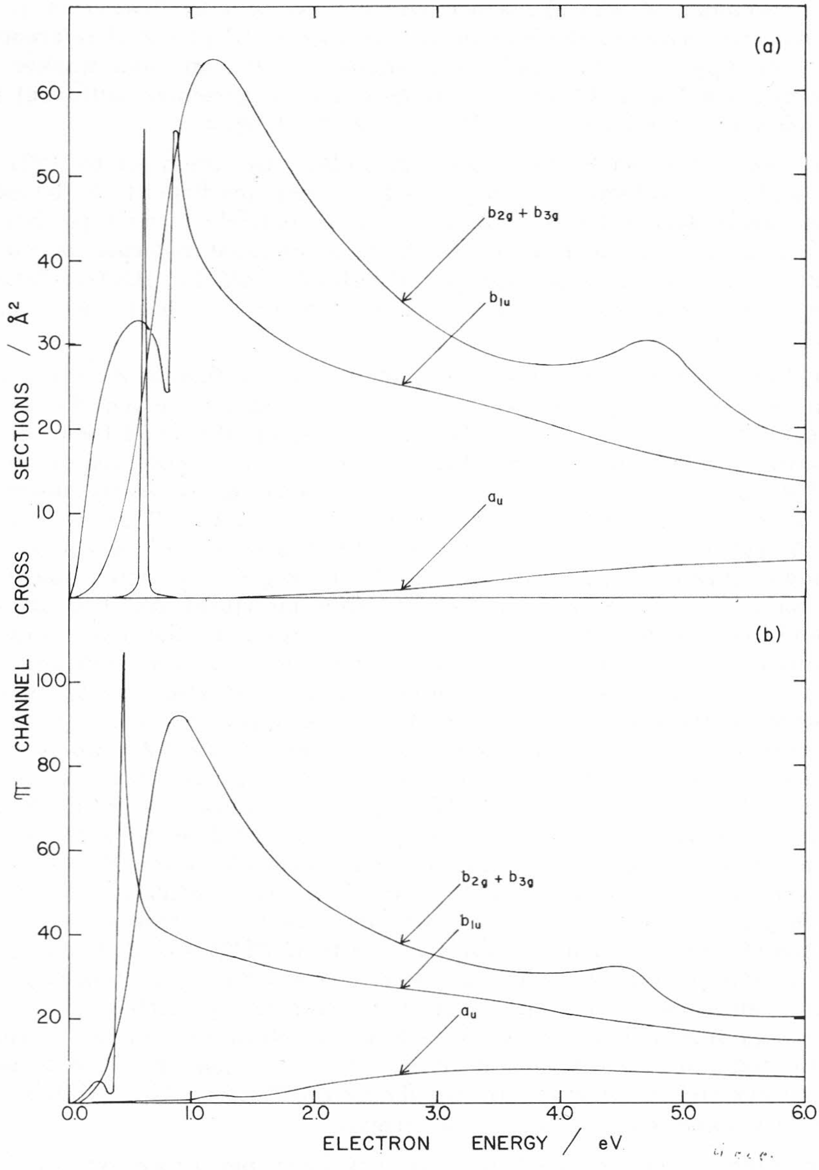

Figure 3. Comparison of theoretical π type channel cross sections, σ_p, for (a) PDFB and (b) TTFB.

the *p*, *d*, and *f*π type orbitals to mix. As a result, the *p*, *f*π type levels which are primarily derived from the two lowest unoccupied π* orbitals in benzene become slightly bound and the strong, broad, structureless resonance seen at 0.8 eV (Figure 2c) is interpreted as due to electron capture in an $e''\pi$ type orbital which is mainly diffuse and made up of *d*π type waves (Table III) in the outer sphere. It is followed by a broader *p*, *f*π resonance predicted to have a maximum at 2.25 eV, which was not assigned by Frazier *et al.*[23] but is clearly discernable in the ETS derivative spectra (Figure 2 of reference 19). Finally the upper π^* level (a_2'') is predicted to give an even weaker (than observed) resonance at 4.2 eV but energetically in agreement with that found experimentally at 4.5 eV (see reference 19 for details).

The calculation on HXFB (Figure 2f) follows the trend set by TFB. Both the $p\sigma$ and lower valence π^* energy levels are now predicted to be bound and the resonance seen at 0.4 eV is predicted to be entirely of $d\pi$ type; however, the resonance seen at about 4.5 eV in all the substituted molecules and usually attributed only to the upper valence π^* orbital could for HXFB (Table III) be due to a σ^* (e_{1u}) orbital or due to a superposition of both the σ^* and π^* type resonances.

In TTFB the two $p\sigma$ resonances noted close to threshold in the PDFB system become now very strong ($\sigma_p = 1070$ Å^2) and are thought by us to be responsible for the steep slope of the ETS coming off threshold for both TTFB and pentafluorobenzene (PTFB) (Figures 2d and e) as observed by Frazier *et al.*[23] An additional structureless region of absorption is clearly observed in the ETS between 1.0 and 1.5 eV for both TTFB and PTFB (Figures 2d and e). In the TTFB a lower energy resonance, with a band center maximum at 0.5 eV, shows vibrational fine structure, while the higher one noted above, with inflection at 1.3 eV, is broader and possesses no vibrational fine structure. It would be tempting to assign these respectively to the two valence π^* resonances, due to electron capture by orbitals of b_{1u} and a_u symmetry, with channel energies calculated to be at 0.44 eV and 1.2 eV respectively. However, the second of these resonances, namely the one appearing in the a_u channel, has a very low and broad total cross section (Figure 3b) compared to the a_u type resonance seen in PDFB (Figure 3a). This can also be seen from the data given in column six of Table III. This a_u channel resonance in TTFB seems to be a very weak diffuse type $f\pi$ resonance as opposed to the expected sharp valence type a_u π^* orbital which appears bound (0.39 eV) in our EA calculations (Table IV). The scattering calculations do, however, predict two diffuse and nearly degenerate ($b_{2g} + b_{3g}$) $d\pi$ type orbitals to be in the energy region where the broad structureless band is observed for both TTFB and PTFB; moreover, as can be seen in Figure 3b, the $d\pi$ resonance has a cross section two orders of magnitude greater than the a_u channel resonance predicted to be in this same energy region. Thus, there seems to be no alternative for us to assigning the observed loss in electron transmission in this region in TTFB to be due to temporary electron capture by two Rydberg diffuse $d\pi$ type orbitals rather than by the expected π^* valence type orbital.

Although actual calculations have not been performed on PTFB, the observed ETS (Figure 2e) can be interpreted by analogy with the assignments made for TTFB. As can be seen in the ETS derivative curve (Figure 2e) there is a very steep fall off with intensity at very low kinetic (near zero) energies. By analogy to TTFB we assign this phenomenon to the presence of the two sharp resonances due to electron capture in two $p\sigma$ orbitals (*i. e.*, the two channels of $b_{2u} + b_{3u}$ symmetry). In the 0.5—1.0 eV region there is a broad resonance predicted to be due to the valence π^* level of b_1 type symmetry. Our calculations suggest the observed broadening compared to TTFB results

TABLE IV

Stable Negative Ion States of the Fluorinated Benzenes

Molecule	Symmetry	Type*	OSMSXα/eV**	Exp./eV***
PDFB	b_{1u}	$p\pi$	0.05	
(D_{2h})	a_g	$s\sigma$	0.20	
TFB	e''	π^*	0.11	
(D_{3h})	a_2''	$p\pi$	0.26	
	a_1'	$s\sigma$	0.77	
TTFB	a_u	π^*	0.39	
(D_{2h})	b_{1u}	$p\pi$	0.53	
	a_g	$s\sigma$	1.10	
HXFB	a_{2u}	$p\pi$	0.08	
(D_{6h})	e_{1u}	$p\sigma$	0.42	
	e_{2u}	π^*	1.26	
	a_{1g}	$s\sigma$	1.77	1.8 ± 0.3

* Classifications used here are the same as in Table III (column 3).

** The sign convention used here for the energies is *positive* for a bound (stable) state. Thus the largest entry for each case in this column yields the EA of the molecule.

*** See Ref. 37.

from the allowed mixing of p and d waves within the b_1 channel by C_{2v} symmetry. This resonance is then followed by an even broader structureless resonance predicted to be the $d\pi$ levels. The final resonance seen in the 4.5 eV region is, as usual, assigned as being due to the upper π^* level. These assignments are all summarized in Table III.

BOUND ELECTRON AFFINITIES

The only experimental value for bound EAs in the fluorosubstituted benzenes is the value for HXFB.[37] The experimental value agrees very well with the calculated value for the totally symmetric diffuse state (Table IV). This state undoubtedly has a very short life time compared to the π^* valence negative ion state predicted to lie just above it (Table IV), and it is possible that the experimental measurements refer to this state.

The results in Tables III and IV show a dramatic increase in the stability of the π^* valence state as the number of fluorine atoms in the molecule increases. Both experiment and theory show clearly that the π^* valence states are unbound in benzene and PDFB, but contrary to current thinking,[23,30] the OSMSXα calculations predict that in the more heavily fluorinated molecules there are multiple bound states, one of which is a long lived π^* valence state. It should be noted that our prediction of bound states in molecules for which the Hartree-Fock method, as usually applied, predicts only unbound states is a feature of the OSMSXα method, and experimental studies on the existence or non-existence of bound negative ion states are badly needed to test these predictions.

CONCLUSIONS

The work described in this paper shows that the overlapping spheres MSXα method is capable of producing values for the IPs, EAs, and the ETS of benzene and a number of its fluorinated derivatives which are in good agreement with experiment.[22,23,30] The good agreement obtained is somewhat unexpected here since it is often argued that any weakness in the spherical averaging procedure used in the MSXα methodology would show up in planar molecules such as the substituted benzenes. The work described in reference 34 also confirms our conclusions that the spherical averaging procedure used in this method may not be too bad provided overlapping atomic spheres are used.

The IP assignments (Table I and II) are for the most part in agreement with previous assignments made using the heavily parameterized HAM/3 method. This finding may perhaps be regarded as offering some justification that both our assignments and the assignments obtained using the HAM/3 method are substantially correct, within the limits of the one electron model.

The assignments for the resonances observed in the ETS of the fluoro-substituted benzenes are very different from those reported previously.[23,30] The latter assignments were made only in terms of π^* orbitals whereas the OSMSXα method predicts that strong resonances can be produced by temporary electron capture in orbitals which are diffuse, *i. e.* more than 70% outer sphere partial wave character and of Rydberg ($l = 2$) character, and hence would not even be considered as possibilities in models based upon virtual orbital energies produced from HFR calculations on neutral molecules using small basis sets. However these novel assignments should be regarded as tentative until further work is completed on other systems.

APPENDIX

Asbrink *et al.* have recently reported studies on the He II PES of *p*-benzoquinone (PBQ) and tetrafluorobenzoquinone (TTFBQ).[36] In order to compare their observed PES to their HAM/3 calculations they related the intensity distribution of the He II PES, in different energy regions, to the number of ionisations in that region. Although this is not an exact relationship they claim that they have found it to be valid for »numerous spectra«.[35] In this appendix we compare their results for these two molecules with the results of our earlier OSMSXα calculations on the IPs of these two molecules.[31]

In Table V are compared the OSMSXα results for PBQ with the HAM/3 results and with the experimental IPs. The numbers in column six represent the relative areas of the different energy regions as reported.[36] The number of ionisations predicted by the OSMSXα method for all energy regions in both molecules agree exactly with the experimental estimates, although the agreement between the OSMSXα results and theory for the second and third IPs in Table V is unusually bad. The detailed assignments given by the OSMSXα (column 1) and HAM/3 (column 4) methods differ considerably because sets of levels which are close together often have a different order in the two methods. One unusual feature of the results in Table V is the poor agreement with experiment given by the HAM/3 method for the third band envelope. On the other hand, the OSMSXα method fits quite well, but with a diferent order in the levels.

TABLE V

*IP Assignments for PBQ**

Orbital	OSMSXα	Orbital**	HAM/3***	Exp.***	Rel. Area***
	eV		eV	eV	
1 b_{3g}	13.02	3 b_{1g}	13.53	13.5	1
3 b_{1g}	13.23	1 b_{3g}	13.84	14.3	5
1 b_{1u}	13.53		14.46	14.8	
7 b_{2u}	14.70		14.56	14.9	
4 b_{3u}	14.89	8 a_g	14.62	15.0	
8 a_g	15.72	4 b_{3u}	15.35	15.5	
6 b_{2u}	16.73	7 a_g	15.51	16.2	3
7 a_g	16.75	3 b_{3u}	15.76	16.7	
3 b_{3u}	17.06	6 b_{2u}	16.29	17.0	
2 b_{1g}	18.92	6 a_g	18.41	19.5	2
6 a_g	19.48	2 b_{1g}	19.48	20.1	
5 b_{2u}	20.86		21.79	22.0	1
2 b_{3u}	25.16		24.18		
5 a_g	26.11		26.28		

* The four lowest IPs in the 10—12 eV region are not considered here. Although generally agreed that there are four IPs in this energy region, the individual assignment of each peak is a matter of great controversy because these calculated IPs are unusually sensitive to the method employed and to the geometry used. See Refs. 31 (1979).

** Assignment from Ref. 36 is given here only when different from OSMSXα assignment.

*** Taken from Ref. 36.

The results for TTFBQ are given in Table VI; again there is a good correlation between the predicted number of IPs and the experimentally determined relative areas. An exception to this is the last IP of the four IPs (the 11 b_{2u} orbital) associated with the four nF orbitals. From *both* the OSMSXα and HAM/3 results one is tempted to place this IP under the peak at 16.2 eV along with the 12 a_g (nF) orbital. However the measurements of relative areas indicate this peak should be assigned to a single ionisation and the next band envelope to five ionisations, as given in Table VI.

It is particularly noteworthy that for TTFBQ the calculations predict correctly the presence of the four πF ionisations in the energy region between 16.0 and 17.5 eV and the nF ionisations in the 15.5 — 16.5 eV region. This correct placement of the fluorine ionisations in this molecule lends confidence to the assignments of Table I for the fluorobenzenes.

Acknowledgements. — This research was supported by the National Science Foundation of the USA through Grant No. CHE 8207040. A generous grant of computer time from the University of Tennessee Computing Center is also gratefully acknowledged.

TABLE VI

*IP Assignments for TTFBQ**

Orbital	OSMSXα eV	Orbital**	HAM/3*** eV	Exp.*** eV	Rel. Area***
2 b_{3g}	14.68		14.67	14.9	3
2 b_{1u}	14.91		14.75	15.1	
7 b_{3u} (nF)	15.47	(nF)	14.78	15.5	
6 b_{1g} (nF)	15.54	11 a_g (nF)	14.92	15.7	1
11 a_g (nF)	15.85	6 b_{1g} (nF)	15.55	16.2	1
10 b_{2u} (nF)	15.94	(nF)	15.80	16.7	5
1 a_u (πF)	16.43	10 b_{2u}	16.08		
1 b_{3g} (πF)	16.51	10 a_g	16.25		
1 b_{2g} (πF)	16.97	1 a_u (πF)	16.37		
1 b_{1u} (πF)	17.25	1 b_{3g} (πF)	16.71	17.5	
5 b_{1g}	18.05	1 b_{2g} (πF)	17.58	17.9	3
9 b_{2u}	18.29	5 b_{1g}	17.65		
10 a_g	18.38	1 b_{1u} (πF)	18.13	18.5	
6 b_{3u}	19.16		18.67	19.0	4
8 b_{2u}	19.90	9 a_g	18.97		
9 a_g	20.47	5 b_{3u}	19.18		
5 b_{3u}	20.64	8 b_{2u}	19.52		
4 b_{1g}	21.79	8 a_g	20.51	21.5	
8 a_g	21.94	4 b_{1g}	21.33	22.5	
7 b_{2u}	23.24		23.62	23.8	
4 b_{2u}	27.43		25.68	25.6	
7 a_g	28.38		27.99		

* The four lowest IPs which appear here in the 10—12 eV region are omitted for the same seasons given in the corresponding footnote of Table V.

** Assignment from Ref. 36 is given here only when different from OSMSXα assignment.

*** Taken from Ref. 36.

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SAŽETAK

Studij utjecaja perfluoroefekta na ionizacijske potencijale i elektronske transmisijske spektre fluorsupstituiranih benzena s pomoću Xα-metode višestrukog raspršenja u aproksimaciji prekrivanja atomskih kugli (OSMS-Xα)

John E. Bloor i Ronald E. Sherrod

Primijenjena je Xα-metoda višestrukog raspršenja u približenju prekrivanja atomskih kugli za studij utjecaja perfluoroefekta na ionizacijske potencijale (IP) i elektronske afinitete (EA) supstiutiranih benzena. Osim IP i EA razmatrani su i elastični udarni presjeci za raspršenje elektrona na benzenu, para-difluorbenzenu, 1,3,5-trifluorbenzenu, 1,2,4,5-tetrafluorbenzenu i heksafluorbenzenu (HXFB). Rezultati za IP slažu se vrlo dobro s eksperimentalnim mjerenjima, ali se znatno razlikuju u asignaciji spektara od prethodnih teorijskih rezultata dobivenih s pomoću Hartree--Fockova računa s minimalnim osnovnim skupom funkcija. Udarni presjeci također se dobro slažu s iskustvom, za razliku od ostalih teorijskih rezultata. Pri tome je druga po redu snažna rezonancija interpretirana kao kratkoživuće stanje negativnog iona koji se dobiva zahvatom elektrona u difuznu Rydbergovu orbitalu d_π-tipa. HXFB je jedina molekula u seriji za koju je izmjeren EA (1,8 eV) što se dobro slaže s izračunanom vrijednošću od 1,7 eV.