

# Semi-empirical Parameters in $\pi$ -Electron Systems

## XII. Fluorine Substituents

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The Pariser-Parr-Pople method has been modified to include fluorine substituents and the extended method has been applied to fluoroethylenes and fluorobenzenes. Calculations of  $\pi$ -electron charge densities, bond lengths, ionization potentials, and electronic transitions for these compounds are presented.

### I. INTRODUCTION

In a series of earlier papers<sup>1-11</sup> the scheme suggested by Roos and Skancke<sup>1</sup> for the semi-empirical parametrization within the Pariser-Parr-Pople approximation has been used to determine parameters appropriate to different  $\pi$ -electron systems: hydrocarbons<sup>1,2</sup> and molecules with nitrogen,<sup>3</sup> chlorine,<sup>4</sup> oxygen,<sup>5,6</sup> sulfur,<sup>7</sup> and bromine atoms,<sup>8</sup> the nitro and nitroso groups,<sup>9</sup> the nitrogen-nitrogen bond and nitrogen-methyl bond<sup>10</sup> and the  $\sigma$  lone pairs of some nitrogen heterocycles.<sup>11</sup> In a study of barriers to internal rotation in fluorobiphenyls, preliminary values of fluorine parameters were evaluated by Farbrot and Skancke.<sup>12</sup> In the present paper the problem of fluorine parameters is examined in more detail and parameters have been determined which are applicable in a more general context.

According to the above-mentioned scheme<sup>1</sup> the parameters are chosen to give the best possible fit between calculated and experimental ionization potentials and singlet transitions of a few standard molecules. Then these parameter values have been tested on a set of other molecules. The test molecules include polyfluoroderivatives of ethylene and benzene as well as benzene derivatives containing both fluorine and other "heteroatoms" such as Cl, Br, OH, and CH<sub>3</sub>.

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## II. METHOD

The method applied for the evaluation of the semi-empirical parameters, and the notations and equations used for the determination of the various integrals have been presented in previous papers<sup>1-11</sup> and will not be repeated here.

The self-consistent field molecular orbitals have been calculated by means of a computer program, SCF-OPSZDO, written by B. Roos and M. Sundbom. This program also calculates the energy levels of excited states by mixing all configurations obtained from single excitations. The computer IBM 360/75 at Stockholm's Data central has been used for the present calculations.

## III. FLUORINE PARAMETERS

The standard molecules chosen for this study were vinyl fluoride and fluorobenzene. The experimental information used in the numerical evaluation of the semi-empirical parameters were the first ionization potential for vinyl fluoride and fluorobenzene, the lowest singlet-singlet transition for the vinyl fluoride and the three lowest transitions for fluorobenzene. The parameters to be determined for the F atom and the C-F bond are:

$$\beta_{CF} = \beta_{CF}^{\circ} + \delta_{CF}^{\beta} (R_{CF} - R_{CF}^{\circ}) \quad (1)$$

$$\gamma_{CF} = \gamma_{CF}^{\circ} + \delta_{CF}^{\gamma} (R_{CF} - R_{CF}^{\circ}) \quad (2)$$

$$W_F = W_F^{\circ} + \delta_{CF}^W (R_{CF} - R_{CF}^{\circ}) \quad (3)$$

and  $\Delta W_C^{\circ}(F)$  in

$$W_C = W_C^{\circ} + \sum_{\nu=1}^3 q_{\nu} [\Delta W_C^{\circ}(\nu) + \delta_{CF}^W (R_{CF} - R_{CF}^{\circ})] \quad (4)$$

In these expressions  $\delta_{CF}^{\beta}$ ,  $\delta_{CF}^{\gamma}$  and  $\delta_{CF}^W$  have been assumed to be equal to the corresponding values for a carbon-carbon bond. For the standard length of a bond between  $sp^2$  hybridized carbon and fluorine the value  $R_{CF}^{\circ} = 1.340 \text{ \AA}$  has been adopted. The one-center two-electron Coulomb repulsion integral  $\gamma_{FF}$  is determined by spectroscopic data in the same way as the  $\gamma_{CC}$ .<sup>13</sup> The values obtained are 11.97 eV and 22.36 eV for C and F, respectively.

Table 1. Semi-empirical parameters.

Carbon parameters from Ref. 2	Fluorine and fluorine-carbon parameters
$R_{CC}^{\circ} = 1.397 \text{ \AA}$	$R_{CF}^{\circ} = 1.340 \text{ \AA}$
$\gamma_{CC} = 11.97 \text{ eV}$	$\gamma_{FF} = 22.36 \text{ eV}$
$\gamma_{CC}^{\circ} = 6.91 \text{ eV}$	$\gamma_{CF}^{\circ} = 5.99 \text{ eV}$
$\delta_{CC}^{\gamma} = -3.99 \text{ eV/\AA}$	
$\beta_{CC}^{\circ} = -2.42 \text{ eV}$	$\beta_{CF}^{\circ} = -1.36 \text{ eV}$
$\delta_{CC}^{\beta} = 3.05 \text{ eV/\AA}$	
$W_C^{\circ} = -9.84 \text{ eV}$	$W_F^{\circ}(C) = W_F^{\circ} + \Delta W_F^{\circ}(C) = 16.77 \text{ eV}$
$\Delta W_C^{\circ} = 0.07 \text{ eV}$	$\Delta W_C^{\circ}(F) = -0.68 \text{ eV}$
$\delta_{CC}^W = 9.22 \text{ eV/\AA}$	

The two-center two-electron integrals for non-nearest neighbours were estimated by the ball approximation,<sup>14</sup> using diameters of the spheres based on the orbital exponents of Duncanson and Coulson.<sup>15</sup> These diameters are 1.47 Å for carbon and 0.90 Å for fluorine. As the parameters for the C–C bond are taken from earlier papers,<sup>1,2</sup> there are just four parameters to be determined:  $\beta_{CF}^\circ$ ,  $\gamma_{CF}^\circ$ ,  $W_F^\circ$ , and  $\Delta W_C^\circ(F)$ . The resulting parameters and those used for carbon are listed in Table 1.

Farbrot and Skancke<sup>12</sup> found a set of parameters very similar to ours with exception of  $W_F^\circ(C)$ . The difference between our value  $W_F^\circ(C) = -16.77$  eV and their values  $W_F^\circ(C) = -11.08$  ( $-12.13$ ) eV is mainly reflected in the value calculated for the ionization potential of the  $\pi$ -lone-pair of the fluorine atom. The large difference in the  $W_F^\circ$  value did not change the predicted lowest transition energies and first ionization potentials significantly (*cf.* Ref. 12).

#### IV. RESULTS AND DISCUSSION

1. *Input geometries.* Fig. 1 shows the direction of  $x$  and  $y$  axes, the polarization angle  $\phi$  and the numbering of positions. Information on input bond distances and angles is given in Table 2.

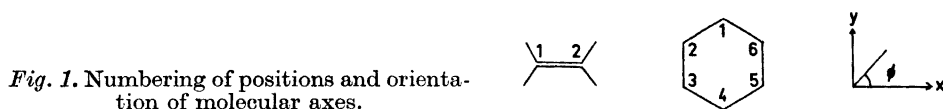


Table 2. Input geometries used for the calculations. Geometries given in the references have been modified as discussed in the text.

Molecule	$R_{CC}(\text{Å})$	$R_{CF}(\text{Å})$	$\angle$	Ref
Ethylene	1.337			
Benzene	1.397		$\angle CCC = 120^\circ$	
Vinyl fluoride	1.330	1.348	$\angle CCF = 121^\circ$	16
1,1-Difluoroethylene	1.315	1.322	$\angle FCF = 109^\circ$	17
<i>cis</i> -Difluoroethylene	1.330 (1.324) <sup>a</sup>	1.348 (1.337) <sup>a</sup>	$\angle CCF = 121^\circ$ ( $122^\circ 9'$ )	17
<i>trans</i> -Difluoroethylene	1.330	1.348	$\angle CCF = 121^\circ$	
Tetrafluoroethylene	1.313	1.313	$\angle FCF = 114^\circ$	18
Monofluorobenzene and remaining fluorobenzenes	1.397	1.354	$\angle CCF = 120^\circ$	19

<sup>a</sup> Values from Ref. 17.

Laurie<sup>16,17</sup> has determined the geometry of vinyl fluoride, 1,1-difluoroethylene, and *cis*-difluoroethylene by microwave spectroscopy. The distances and angles determined for vinyl fluoride have also been used for the *trans*

and *cis* forms, since no values have been published for the *trans* form. The geometry of tetrafluoroethylene has been determined by Karle and Karle<sup>18</sup> by electron diffraction.

For monofluorobenzene and the remaining fluorobenzenes a regular benzene ring was assumed and all the C–F distances were put equal to the C–F distance in monofluorobenzene. The structure of monofluorobenzene has been determined very accurately from microwave spectroscopy by Nygaard *et al.*<sup>19</sup> For the benzene derivatives with several kinds of heteroatoms, a regular carbon hexagon has been assumed. Standard values have been used for the C–X bonds; C–Cl, 1.718 Å; C–Br, 1.88 Å; C–OH, 1.35 Å; and C–CH<sub>3</sub>, 1.52 Å.

Table 3. Calculated  $\pi$  electron densities and bond orders. The numbering of the atoms is given in Fig. 1. The fluorine subscript refers to the carbon atom to which it is bonded; see Fig. 1.

Molecule	Atom	$\pi$ -Electron density	Bond	Bond order
Vinyl fluoride	1	1.052	1–2	0.994
	2	0.959		
	F <sub>1</sub>	1.989	C–F	0.101
1,1-Difluoroethylene	1	1.145	1–2	0.979
	2	0.877		
	F	1.989	C–F	0.099
<i>cis</i> -Difluoroethylene	1	1.011	1–2	0.989
	F	1.989	C–F	0.107
<i>trans</i> -Difluoroethylene	1	1.011	1–2	0.988
	F	1.988	C–F	0.107
Tetrafluoroethylene	1	1.031	1–2	0.969
	F	1.985	C–F	0.122
	1	1.048	1–2	0.663
	2	0.983	2–3	0.667
	3	1.001	3–4	0.666
<i>m</i> -Difluorobenzene (1,3)	4	0.993	C–F	0.092
	F <sub>1</sub>	1.991		
	1	1.049	1–2	0.664
	2	0.966	3–4	0.663
	4	0.976	4–5	0.667
<i>p</i> -Difluorobenzene (1,4)	5	1.002	C–F	0.092
	F	1.991		
	1	1.042	1–2	0.663
	2	0.984	2–3	0.667
	F	1.991	C–F	0.094
<i>sym</i> -Trifluorobenzene	1	1.050	1–2	0.663
	2	0.959	C–F	0.091
	F <sub>1</sub>	1.991		

Table 3. Continued.

1,2,4-Trifluorobenzene	1	1.025	1-2	0.659
	2	1.032	2-3	0.664
	3	0.966	3-4	0.663
	4	1.043	5-6	0.666
	5	0.977	1-F	0.095
	6	0.985	2-F	0.094
	F	1.991	4-F	0.093
1,2,4,5-Tetrafluorobenzene	1	1.026	1-2	0.660
	3	0.967	2-3	0.664
	F	1.991	C-F	0.095
1-F-3-Cl-Benzene	1	1.047	1-2	0.664
	2	0.997	2-3	0.660
	3	0.989	3-4	0.660
	4	1.007	4-5	0.667
	5	0.999	5-6	0.666
	6	0.989	6-1	0.663
	F	1.991	1-F	0.092
	Cl	1.981	3-Cl	0.140
1-F-4-Br-Benzene	1	1.058	1-2	0.662
	2	0.981	2-3	0.669
	3	1.022	3-4	0.656
	4	0.975	1-F	0.090
	F	1.991	4-Br	0.175
	Br	1.970		
1-F-2-OH-Benzene	1	1.145	1-2	0.636
	2	0.811	2-3	0.635
	3	1.097	3-4	0.674
	4	0.985	4-5	0.661
	5	1.040	5-6	0.668
	6	0.974	6-1	0.662
	F	1.993	1-F	0.079
	O	1.955	2-O	0.229
1-F-4-CH <sub>3</sub> -Benzene	1	1.055	1-2	0.662
	2	0.981	2-3	0.669
	3	1.017	3-4	0.658
	4	0.981	1-F	0.091
	F	1.991	4-C	0.155
	CH <sub>3</sub>	1.976		

2. Charge densities, bond orders and bond lengths.  $\pi$ -Electron densities and bond orders are given in Table 3. From the bond orders ( $p_{\mu\nu}$ ) one can estimate the bond lengths for the C-C and C-F bonds, using the following relationships:<sup>20,21</sup>

$$R_{CC} = 1.517 - 0.18 p_{CC} \quad (5)$$

$$R_{CF} = 1.380 - 0.18 p_{CF} \quad (6)$$

The C-C distances obtained from (5) are 1.338 Å for vinyl fluoride, 1.339 Å for *cis*- and *trans*-difluoroethylene, 1.341 Å for 1,1-difluoroethylene, and 1.343 Å for tetrafluoroethylene. These bond lengths should be compared with those given in Table 2 and used as input. However, it should be noted that

the parameters of eqn. (5) have been obtained by assuming a pure double bond to be 1.337 Å. Therefore, the formula can never lead to distances shorter than this value. Moreover, the very short C–C distances observed, *e.g.* for tetrafluoroethylene, are likely to have the same origin as the shortening of C–F bonds in polyfluorocompounds, *i.e.* in the density distribution of the  $\sigma$  electrons. In the fluorobenzenes the C–C distances obtained from (5) are 1.397 or 1.398 Å in very satisfactory agreement with experiments.

The C–F distances obtained from (6) vary between 1.358 Å and 1.364 Å. These values are in good agreement with experiments in the case of fluorobenzenes but the agreement is not so good in the case of fluoroethylenes. The experimental values for the C–F bond length in these latter molecules vary between 1.313 Å and 1.348 Å. The short distances in the polyfluoroethylenes most likely depend on the exceptional electronegativity of fluorine. This effect is obvious in such saturated fluorine compounds as  $\text{CHF}_3$  and  $\text{CF}_4$ . Here, the C–F distances<sup>22</sup> are 1.332 and 1.323 Å as compared to 1.385 Å in  $\text{CH}_3\text{F}$ . These special effects are not accounted for by eqn. (6).

Experimental evidence shows that the fluorine atoms of the asymmetric fluoroethylenes increase the electron density on the  $\beta$  carbon. Chemical evidence also shows that fluorine has an *ortho*, *para*-directing effect.

Within the present computational scheme, the  $\pi$ -electron densities indicate that fluorine should have a *meta*-directing effect and in the case of the fluoroethylene, the  $\alpha$  carbon has the largest negative charge. Similar results were found by Grabe<sup>4</sup> in the case of chlorine substituents, and by Seybold and Fischer-Hjalmars<sup>8</sup> in the case of bromine substituents. The reason for this, as Seybold and Fischer-Hjalmars pointed out, is the charge build-up on the atom  $\text{C}_1$ , to which the fluorine is attached. The value of  $q_{\text{C}}$ , in fluorobenzene, is 1.048, which means that although the fluorine shoves 0.009 of an electron onto the ring, this is cancelled by the charge build-up on  $\text{C}_1$ , and this is originated from the value of  $\Delta W_{\text{C}}(\text{F})$ .

Looking at the result for chlorobenzene,<sup>4</sup> bromobenzene,<sup>8</sup> and fluorobenzene, one sees that fluorine contributes 0.009, chlorine 0.023, and bromine 0.044 of an electron to the ring  $\pi$ -system, this being in agreement with the electronegativity of the elements.

Table 4. Electronic populations of  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_3\text{F}$  from *ab initio* calculations.<sup>23</sup>

Populations	Carbon atom			Fluorine atom
	of $\text{C}_2\text{H}_4$	$\alpha$ of $\text{C}_2\text{H}_3\text{F}$	$\beta$ of $\text{C}_2\text{H}_3\text{F}$	
Gross atomic: total	6.131	5.684	6.192	9.385
$\sigma$	5.137	4.684	5.133	7.454
$\pi$	0.994	0.999	1.059	1.931
Net atomic: total	4.736	4.507	4.932	9.141
$\sigma$	3.998	3.756	4.121	7.221
$\pi$	0.738	0.751	0.811	1.920

Table 5. Calculated  $\pi$ -electron dipole moments and experimentally observed total dipole moments (Debyes).

Molecule	Calculated $\mu_\pi$		Observed $\mu_{\text{total}}$
	Semi-empirical	<i>Ab initio</i> <sup>23</sup>	
Vinyl fluoride	0.22	0.77	1.427
1,1-Difluoroethylene	0.69		1.366
<i>cis</i> -Difluoroethylene	0.12		2.42
Fluorobenzene	0.13		1.66, 1.61
<i>m</i> -Difluorobenzene	0.13		1.51
1,2,4-Trifluorobenzene	0.12		
1-F-3-Cl-Benzene	0.38		
1-F-4-Br-Benzene	0.64		
1-F-2-OH-Benzene	1.22		
1-F-4-CH <sub>3</sub> -Benzene	0.47		

In this context it is informative to study the population analysis based on the *ab initio* calculations by Meza and Wahlgren.<sup>23</sup> The values listed in the present Table 4 are derived from their Tables 4 and 5, which contain results for ethylene and fluoroethylene, obtained with the same basis set for carbon and hydrogen. Considering the gross atomic populations it seems as if the  $\beta$  carbon atom of C<sub>2</sub>H<sub>3</sub>F only differed from the carbon atoms of C<sub>2</sub>H<sub>4</sub> by a small gain of  $\pi$  charge (0.065 of an electron). However, a study of the net atomic populations reveals that the electronic distribution around the  $\beta$  carbon has changed drastically. In fact, the total net population has increased by 0.20 of an electron, 0.12 being increased  $\sigma$  population. This result is in complete agreement with the electron distribution indicated by experiments. It is interesting to notice that the  $\sigma$  electrons on the  $\beta$  carbon have been donated by the  $\alpha$  carbon. Moreover this atom is also donating  $\sigma$  electrons to the fluorine. The  $\pi$ -donation by the fluorine is more than counterbalanced by the flow of  $\sigma$  electrons in the opposite direction. It is noticeable that the net  $\pi$ -population of the  $\alpha$  carbon is indeed 0.013 of an electron *larger* than that of carbon in ethylene. This increase is in harmony with that obtained by the present semiempirical calculation. However, it is obvious that the complicated rearrangement of the electronic charge distribution, originating from the substitution of a fluorine atom for a hydrogen atom, cannot be reproduced by any parameter set according to the present scheme. One reason for this is that no parameter in the scheme is related to the  $\sigma$ -density of the  $\beta$  carbon.

A way out of this dilemma would be to modify the whole scheme. However, our purpose is not to find a semi-empirical scheme giving the best possible reproduction of the properties of fluorine compounds. The interesting study of Narayan and Murrell<sup>24</sup> has shown that even the limited goal of reproducing ionization potentials and the shift of the lowest electronic transition of fluorobenzenes requires the introduction of both short-range and long-range inductive parameters. Our aim is rather to find those parameters of the previously adopted scheme<sup>1-11</sup> which will do the best to describe fluorine compounds. Our analysis of the *ab initio* charge distribution shows, as does also the re-

sults of Ref. 24, that we should not expect too much success, in particular not for molecules with several fluorines on the same carbon. Nevertheless it is interesting to analyse the results that can be obtained by the present method.

3. *Dipole moments.* The  $\pi$  contribution to the dipole moments and the observed values of the total dipole moments are given in Table 5. The small  $\pi$  contribution to the dipole moment suggests that the total dipole moment mainly consists of the  $\sigma$ -part. This is in harmony with the result from the *ab initio* calculation<sup>23</sup> on vinyl fluoride, which gave a total moment of 1.85 Debye, the  $\pi$ -part being 0.77 Debye.

4. *Ionization potentials.* The ionization potentials (IP's) are calculated from Koopmans' theorem, which means that they should be compared to the vertical IP's. However, most values found in literature are adiabatic potentials. Therefore, the carbon parameters<sup>1</sup> were determined with reference to such values. For consistency, the fluorine and the carbon-fluorine parameters have also been determined by fitting to adiabatic values. Calculated and observed ionization potentials are collected in Tables 6, 7, and 8.

Table 6. Calculated and experimental lowest ionization potentials and  $\pi$  lone-pair ionization potentials for ethylene derivatives. Energies in eV.

Molecule	Calculated				Observed <sup>a</sup>	
	Semi-empirical lowest lonepair		<i>Ab initio</i> lowest	<i>Ab initio</i> lonepair	lowest	
Ethylene	10.53		10.07 <sup>25</sup>		10.52 <sup>b</sup> , v: 10.51 <sup>33</sup>	
Vinyl fluoride	10.74	17.00	10.22 <sup>23</sup>	18.09 <sup>23</sup>	10.37, <sup>25,26</sup> 10.45, <sup>27</sup> v: 10.58 or 10.77 <sup>26</sup>	
1,1-Difluoroethylene	11.26	17.00			10.30, <sup>25</sup> 10.31, <sup>26</sup> 10.45, <sup>27</sup> v: 10.72 <sup>26</sup>	
<i>cis</i> -Difluoroethylene	10.85	16.93	10.38 <sup>28</sup>	18.02 <sup>28</sup>		
<i>trans</i> -Difluoroethylene	10.85	16.93	10.39 <sup>28</sup>	18.36 <sup>28</sup>		
Tetrafluoroethylene	11.76	17.10			10.12, <sup>25,27</sup> 10.11 <sup>26</sup> v: 10.54 <sup>26</sup>	

<sup>a</sup> Adiabatic, except when marked by v: (vertical).

<sup>b</sup> Used in Ref. 1 for the determination of carbon parameters.

The lowest adiabatic IP's for fluoroethylenes (Table 6) have been determined from photoionization by Bralsford *et al.*<sup>25</sup> Very recently, Lake and Thompson<sup>26</sup> have determined both adiabatic and vertical IP's for vinyl fluoride, 1,1-difluoroethylene, and tetrafluoroethylene from photoelectron spectroscopy. They also report several higher ionization potentials for each of these molecules but without any assignment. Their vertical ionization potentials for vinyl fluoride are 10.58, 13.79, 14.51, 16.77, and 17.97 eV. Meza and Wahlgren<sup>23</sup> have compared these values with the orbital energies of their *ab initio* calculation on vinyl fluoride. From this comparison they conclude that the potential of 16.77 eV should originate from ionization of the fluorine  $\pi$  lone-pair orbital. There is at the present time some controversy about where



Table 7. Calculated semi-empirical values for the lowest and the  $\pi$  lone-pair ionization potentials of benzene derivatives. Energies in eV.

Molecule	Calculated		Observed <sup>a</sup>
	lowest	lonepair	
Benzene	9.24		9.25 <sup>b</sup> , v: 9.40 <sup>30</sup>
Fluorobenzene	9.24	16.91	9.20, <sup>25</sup> 9.21, <sup>29</sup> 9.19, <sup>31</sup> v: 9.40, <sup>31</sup> 9.5 <sup>30</sup>
<i>o</i> -Difluorobenzene	9.28	16.80	9.31, <sup>25</sup> 9.30, <sup>31</sup> v: 9.51 <sup>31</sup>
<i>m</i> -Difluorobenzene	9.28	16.91	9.33, <sup>25</sup> 9.32, <sup>31</sup> v: 9.51 <sup>31</sup>
<i>p</i> -Difluorobenzene	9.40	16.93	9.15, <sup>25,29</sup> 9.20, <sup>31</sup> v: 9.40, <sup>31</sup> 9.50 <sup>30</sup>
1,2,4-Trifluorobenzene	9.28	16.83	9.37, <sup>25</sup> 9.30, <sup>29</sup> 9.31, <sup>31</sup> v: 9.55 <sup>31</sup>
<i>Sym</i> -Trifluorobenzene	9.35	16.94	9.62, <sup>31</sup> v: 9.81 <sup>31</sup>
1,2,4,5-Tetrafluorobenzene	9.31	16.84	9.39, <sup>25</sup> 9.40, <sup>31</sup> v: 9.56 <sup>31</sup>
1,2,3,4-Tetrafluorobenzene	9.34	16.77	9.61, <sup>25,31</sup> v: 9.80 <sup>31</sup>
Hexafluorobenzene	9.44	16.80	9.97, <sup>25</sup> 9.88, <sup>29</sup> 9.93, <sup>31</sup> v: 10.11 <sup>31</sup>
1-F-3-Cl-Benzene	9.00		9.21 <sup>41</sup>
1-F-4-Br-Benzene	8.96		8.99 <sup>41</sup>
1-F-2-OH-Benzene	8.42		8.66 <sup>41</sup>
1-F-4-CH <sub>3</sub> -Benzene	9.00		8.79 <sup>41</sup>

<sup>a</sup> Adiabatic, except when marked by v: (vertical).

<sup>b</sup> Used in Ref. 1 for the determination of carbon parameters.

Table 8. Splitting of the first  $\pi$ -ionization potential of benzene by fluoro substitution. Energies in eV.

Molecule	Calculated	Separation of maxima	
		$\Delta$ IP(adiab.)	Observed <sup>31</sup> $\Delta$ IP(vert.)
Fluorobenzene	0.07	0.41	0.41
<i>o</i> -Difluorobenzene	0.07	0.44	0.44
<i>m</i> -Difluorobenzene	0.07	0.41	0.41
<i>p</i> -Difluorobenzene	0.14	0.44	0.64
1,2,4-Trifluorobenzene	0.13	0.59	0.59
1,2,4,5-Tetrafluorobenzene	0.14	0.69	0.69
1,2,3,4-Tetrafluorobenzene	0.08	0.32	0.32

the  $\pi$  lone-pair IP's lie. Turner *et al.*<sup>32</sup> and Clark and Frost<sup>29</sup> suggest that for fluorobenzenes these IP's lie in the 9–15 eV region of the spectra. On the other hand, Narayan and Murrell<sup>24</sup> believe that the IP's should be found in the 16–19 eV region for both aliphatic and aromatic compounds. This latter point of view is supported by the results of Meza and Wahlgren<sup>23</sup> and has been adopted for the present parameter fitting. Table 6 shows that for all fluoroethylenes the calculated lone-pair IP is close to 17 eV, in excellent agreement with the value 16.8 eV.

The lowest ionization potentials of the fluoroethylenes do not agree quite so well with measured adiabatic potentials. However, in view of the much larger difference (0.4 eV) between adiabatic and vertical potentials for the

fluoroethylenes than for ethylene itself (0.1 eV) the calculated values are quite reasonable in all cases with not more than one fluorine at each site. As discussed above, polysubstitution, in particular at a single site, will give rise to effects that cannot be reproduced by the present model.

Table 7 shows the lowest and the lone-pair potentials of benzene derivatives. The calculated lone-pair potentials agree very well with the observed values according to the assignments of Narayan and Murrell.<sup>24</sup> The calculated lowest IP's are all found in the same region as the observed values. It is interesting to notice that all the observed vertical potentials are very close to the vertical IP of benzene with the exception of hexafluorobenzene with an IP 0.8 eV higher than that of benzene. The calculated values indicate the same trend, although the spread is too small, only 0.2 eV.

The lowest IP of benzene originates from a degenerate  $\pi$ -orbital. This degeneracy is removed in benzene derivatives of sufficiently low symmetry. This effect in case of fluorobenzenes has been discussed in detail by Narayan and Murrell<sup>24</sup> and is well reproduced by their model. The observed splitting is compared to our calculated splitting in Table 8. Again, the spread is too small. However, it is gratifying to notice that there is a clear parallelism between calculated and observed values. The IP's of compounds with mixed substituents are shown in Table 7 and the agreement between the calculated and experimental values is satisfactory.

5. *Absorption spectra.* Results from calculations of transition frequencies  $\nu$ , oscillator strengths  $f$ , and polarization directions are listed in Tables 9 and 10. The tables also include pertinent experimental results, reported in literature.

The only publication of gas phase absorption spectra of fluoroethylenes seems to be the one by Belanger and Sandorfy.<sup>34</sup> These authors have measured the far UV spectra between 2000 and 1150 Å. They found both valence shell transitions and Rydberg bands. The  $\pi \rightarrow \pi^*$  bands were identified by their intensity and breadth. Their reported values of the maxima are reproduced in our Table 9. These values can hardly be interpreted by any simple theoretical

Table 9. Calculated and experimental electronic singlet-singlet transitions for the fluoroethylenes. Energies in  $\text{cm}^{-1} \times 10^{-3}$  (kK).

Molecule	Present calculation			Observations in vapor phase <sup>34</sup>	
	Energy	$f^a$	Pol. <sup>a</sup>	$\nu_{\text{max}}$	Intensity
Ethylene	61.53	0.60	$x$	61.70 <sup>b</sup>	$f = 0.34$
Vinyl fluoride	60.84	0.60	1.2	60.00 <sup>c</sup>	$\epsilon = 10\ 000$
1,1-Difluoroethylene	60.12	0.58	$x$	60.50	7 900
<i>cis</i> -Difluoroethylene	59.90	0.60	$x$	63.04	7 490
<i>trans</i> -Difluoroethylene	59.90	0.60	2.4	58.75	5 360
Tetrafluoroethylene	57.37	0.59	$x$	71.65	11 370

<sup>a</sup>  $f$  = Oscillator strength; Pol. = Polarization in degrees (see Fig. 1).

<sup>b</sup> The value 61.5 has been used in Ref. 1 for the determination of carbon parameters.

<sup>c</sup> Used in the present paper for the determination of fluorine and carbon-fluorine parameters.

Table 10. Calculated and experimental electronic singlet-singlet transitions for benzene derivatives. Energies in  $\text{cm}^{-1} \times 10^{-3}$  (kK).

Present calculation				Observations			
Energy	$-\Delta\nu^a$	$f^a$	Pol. <sup>a</sup>	Reference, Solvent	Energy	$-\Delta\nu^a$	$f^a$
Benzene							
39.17		Forb.		vapor <sup>35</sup>	39.46		
50.62		Forb.			49.80		
56.15		1.19			56.31		
				hexane <sup>36</sup>	39.4		0.0014
					49.5		0.10
					54.4		0.69
				vapor <sup>37</sup>	39.5 <sup>b</sup>		0.0016
				vapor <sup>38</sup>	50.6 <sup>b</sup>		
					55.9 <sup>b</sup>		
Fluorobenzene							
39.06	0.11	0.002	<i>x</i>	vapor <sup>35</sup>	39.04 <sup>c</sup>	0.42	0.003
50.40	0.22	0.002	<i>y</i>		49.93 <sup>c</sup>	-0.13	0.15
56.01	0.14	1.20	<i>y</i>		56.46 <sup>c</sup>	-0.15	1.43
56.03	0.12	1.18	<i>x</i>				
				vapor <sup>39</sup>	37.82 <sup>d</sup>	0.27	0.009
					39.19 <sup>e</sup>		
				vapor <sup>40</sup>	56.31	0	1.27
<i>m</i> -Difluorobenzene							
38.97	0.20	0.002		59.9	vapor <sup>39</sup>	37.91 <sup>d</sup>	0.18
50.21	0.41	0.001		-29.7			0.010
55.88	0.27	1.18		-29.5		39.28 <sup>e</sup>	
55.89	0.26	1.20		60.5			
<i>p</i> -Difluorobenzene							
38.91	0.26	0.007	<i>x</i>	vapor <sup>39</sup>	36.84 <sup>e</sup>	1.24	0.022
50.17	0.45	0.007	<i>y</i>				
55.87	0.28	1.21	<i>y</i>		38.22 <sup>e</sup>		
55.97	0.18	1.17	<i>x</i>				
<i>sym</i> -Trifluorobenzene							
38.91	0.26	Forb.		vapor <sup>39</sup>	38.53 <sup>d</sup>	-0.44	0.002
50.04	0.58	Forb.					
55.74	0.41	1.20			39.90 <sup>e</sup>		
1,2,4-Trifluorobenzene							
38.83	0.34	0.006	-30.4	vapor <sup>39</sup>	37.12 <sup>d</sup>	0.97	0.019
49.97	0.65	0.005	57.8				
55.74	0.41	1.20	69.5		38.50 <sup>e</sup>		
55.80	0.35	1.19	-21.2				
1,2,4,5-Tetrafluorobenzene							
38.71	0.46	0.008	-60.0	vapor <sup>39</sup>	36.61 <sup>d</sup>	1.48	
49.75	0.87	0.007	29.9				
55.62	0.53	1.18	30.0		37.98 <sup>e</sup>		
55.68	0.47	1.21	-60.0				

<sup>a</sup>  $f$  = Oscillator strength; Pol. = Polarization in degrees (see Fig. 1);

$\Delta\nu$  = Energy shift relative to benzene.

<sup>b</sup> Used in Ref. 1 for the determination of carbon parameters.

<sup>c</sup> Used in the present paper for the determination of fluorine and carbon-fluorine parameters.

<sup>d</sup> 0-0 band.

<sup>e</sup>  $\nu_{\text{max}}$  estimated by the assumption that the shift  $\Delta\nu$  of the maximum is the same as  $\Delta\nu$  measured for the 0-0 band; for benzene  $\nu_{\text{max}}$  is assumed to be 39.46 kK and  $\nu_{00}$  38.09 kK.

model. As an example, the introduction of a second F atom gives rise to shifts of  $\nu_{\max}$  of +0.50 kK in the 1,1-compound, +3.04 kK in the *cis*-, and -1.25 kK in the *trans*-compound. No parameter set within our scheme can reproduce such trends. The agreement between calculated and measured values is therefore only moderate for the polyfluoroethylenes.

Table 10 presents some of our results for benzene derivatives. Since observations on the UV spectra of fluorobenzenes in vapor are very scarce, we only report the calculated values for those molecules where at least some measurement is available. Kimura and Nagakura<sup>35</sup> have published very accurate vapor phase spectra for fluorobenzene in the region of 2200–1550 Å. Sponer<sup>39</sup> has measured the position of the 0–0 band of the lowest electronic transition,  $^1L_b$ , for a series of fluorobenzenes. For fluorobenzene she found a bathochromic shift of this transition, though somewhat smaller than that measured by Kimura and Nagakura.<sup>35</sup> Very recently, Gilbert and Sandorfy<sup>40</sup> have measured the fluorobenzene spectrum in the region 2200–1500 Å. They have observed three  $\pi \rightarrow \pi^*$  transitions but only reported the value of

Table 11. Electronic transitions for some mixed substituted benzenes.<sup>a</sup> Energies in  $\text{cm}^{-1} \times 10^{-3}$

Energy	Present calculation		Pol.	Observations in cyclohexane <sup>b</sup>		
	$-\Delta\nu$	$f$		Energy	$-\Delta\nu$	$\log \epsilon$
1-F-3-Cl-Benzene						
38.75	0.42	0.006	-29.6	38.76 <sup>42</sup>	0.44	2.78
49.73	0.89	0.014	13.3	47.39	1.41	3.93
55.48	0.67	1.22	52.8			
55.64	0.51	1.16	-36.6			
1-F-4-Br-Benzene						
38.75	0.42	0.0004	<i>x</i>	38.61 <sup>43</sup>	0.59	2.74
49.59	1.03	0.040	<i>y</i>	46.08	2.72	3.85
55.48	0.67	1.15	<i>x</i>			
55.49	0.66	1.23	<i>y</i>			
1-F-2-OH-Benzene						
38.05	1.12	0.07	52.2	38.17 <sup>44</sup>	1.03	3.10
49.24	1.38	0.03	-30.3	47.17	1.63	3.76
55.37	0.78	1.20	-38.7			
56.27	-0.12	1.01	50.5			
1-F-4-CH <sub>3</sub> -Benzene						
38.75	0.42	0.0001	<i>x</i>	38.31 <sup>42</sup>	0.89	3.00
49.37	1.25	0.045	<i>y</i>	48.54	0.26	3.86
55.37	0.78	1.13	<i>x</i>			
55.39	0.76	1.19	<i>y</i>			

<sup>a</sup> Parameters for substituents other than fluorine were obtained as follows: Cl, Ref. 4; Br, Ref. 8; OH, Ref. 6; CH<sub>3</sub>, Ref. 2.

<sup>b</sup> Benzene absorption maxima at 39.2 kK (255 m $\mu$ ) and 48.8 kK (205 m $\mu$ ).

$\nu_{\max}$  for the third transition. They did not find any energy shift in this case, for which Kimura and Nagakura<sup>35</sup> report a small hypsochromic shift. This shows that the experimental results are somewhat uncertain. In particular, one cannot always expect a parallelism between the shifts of  $\nu_{\max}$  and of the 0-0 band. With this in mind, our calculated transition energy is found to agree rather well with available experiments. It is interesting that we calculate the largest bathochromic shift of the  ${}^1L_b$  band in the case of 1,2,4,5-tetrafluorobenzenes, where Sponer<sup>39</sup> also has found the largest shift within the series.

For benzene derivatives with mixed substituents (Table 11), the present calculations give good agreement with the experimental (solution) results.

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