

# Chemical structural effects on $\gamma$ -ray spectra of positron annihilation in fluorobenzenes<sup>\*</sup>

F. Wang<sup>1,a</sup>, X.G. Ma<sup>1,2</sup>, L. Selvam<sup>1</sup>, G.F. Gribakin<sup>3</sup>, and C.M. Surko<sup>4</sup>

<sup>1</sup> eChemistry Laboratory, Faculty of Life and Social Sciences, Swinburne University of Technology, P.O. Box 218, Hawthorn, 3122 Victoria, Australia

<sup>2</sup> School of Physics, Ludong University, Yantai, Shandong 264025, P.R. China

<sup>3</sup> Centre for Theoretical Atomic, Molecular and Optical Physics, School of Mathematics and Physics, Queen's University Belfast, Belfast BT7 1NN, Northern Ireland, UK

<sup>4</sup> Physics Department, University of California, San Diego, La Jolla, 92093-0319 California, USA

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**Abstract.** Spectra of  $\gamma$ -ray Doppler shifts for positron annihilation in benzene and its fluoro-derivatives are simulated using low energy plane wave positron (LEPWP) approximation. The results are compared with available measurements. It is found that the Doppler shifts in these larger aromatic compounds are dominated by the contributions of the valence electrons and that the LEPWP model overestimates the measurements by approximately 30%, in agreement with previous findings in noble gases and small molecules. It is further revealed that the halogen atoms not only switch the sign of the charges on carbon atoms that they bond to, but that they also polarize other C-H bonds in the molecule leading to a redistribution of the molecular electrostatic potentials. As a result, it is likely that the halogen atoms contribute more significantly to the annihilation process. The present study also suggests that, while the Doppler shifts are sensitive to the number of valence electrons in the molecules, they are less sensitive to the chemical structures of isomers that have the same numbers and type of atoms and, hence, the same numbers of electrons. Further investigation of this effect is warranted.

## 1 Introduction

Gamma-ray spectra of positron annihilation in various atomic and molecular targets have been studied for many decades [1–11]. However, theoretical description of the interactions between the molecular electrons and the positron in these annihilation processes has lagged experiment, particularly for molecular targets. This is partly because the methodology employed to resolve multicentre molecular problems is far more complex than single centre atomic problems. In particular, positron interactions with bound electrons in molecules also depend on properties unique to molecules, such as the chemical bonds and chemical environment [1,2]. A number of studies related to positron-molecule binding energies [12,13] indicate the importance of molecular properties, such as the permanent dipole moment ( $\mu$ ) and the dipole polarizability ( $\alpha$ ). Furthermore, to solve the Schrödinger equation for a positron and the bound electrons in a molecule simultaneously is a challenging quantum mechanical problem.

Our understanding of positrons and their behaviour in molecules is relatively new and incomplete compared

to more familiar electron problems. For example, there does not exist an appropriate means to model efficiently the additional Coulomb potentials between the positron, the electrons and the nuclei in a molecule. Certain empirical and semi empirical means [12–14] have been employed to explore the connections between molecular properties and the binding energies between positrons and molecules. The study of the  $\gamma$ -ray spectra of positron interaction with bound electron systems can potentially reveal other aspects and properties of the electrons in atoms and molecules that cannot be determined from electron-electron interactions, thus opening up a new avenue to chemistry.

The momentum distributions of the bound electrons are dominant in the annihilation processes involving atoms<sup>1</sup> [2] and molecules [10]. A number of fluorine substituted aromatic derivatives are commercially well known ligands [15–17]. Fluorine is referred to as a “super halogen” atom which serves to polarize the covalent bonds to electropositive atoms. This  $\sigma$  electron-withdrawing and  $\pi$  electron-donating tendency is exhibited, for example, in fluorine substituted benzenes. The selective

<sup>\*</sup> Figure 1S and Table 1S are only available in electronic format at [www.epj.org](http://www.epj.org).

<sup>a</sup> e-mail: [fwang@swin.edu.au](mailto:fwang@swin.edu.au)

<sup>1</sup> F. Wang, X. Ma, L. Selvam, G.F. Gribakin, C.M. Surko, New J. Phys. (under revision).

introduction of a fluoro group into biologically active molecules has gained much attention in medically relevant studies [15,18], due to the following characteristics: (1) the fluorines mimic hydrogen atoms without much distortion in the geometry of the molecule; (2) it is the most electronegative atom; and (3) the strength of the C-F bond exceeds that of the C-H bond, which induces biological activity and chemical stability of the compounds [2]. In fact, fluorobenzenes (FB) and fluorobenzimidazoles (FBZ) have been proposed as novel nucleic acid base analogues to replace nucleobases [19–22].

Experiments on fluorobenzene molecules [3] have clearly indicated that the measured Doppler shifts and annihilation rates depend on the chemical structures and chemical bonds. For example, the measured values of the full width of half maximum (FWHM) of the Doppler shift spectra ( $\Delta\varepsilon$ ) of  $C_6H_5F$ ,  $C_6HF_5$  and  $C_6F_6$  are given by 2.43, 2.89 and 2.95 keV, respectively, and the normalized annihilation rates ( $Z_{eff}$ ) of the three difluorinated isomers of 1,2- $C_6H_4F_2$ , 1,3- $C_6H_4F_2$  and 1,4- $C_6H_4F_2$  are vastly different: 32 800, 13 100 and 13 500, respectively [3]. Clearly, the  $\gamma$ -ray spectra of the difluorobenzene isomers are not only affected by the dipole moment, polarizability and other properties, but they also depend on the details of the chemical structure, such as the chemical bonding and aromaticity. Thus it would be very difficult to understand the process fully without understanding details of the chemistry and chemical bonding environment.

A few decades ago, electron spectroscopy for chemical analysis (ESCA) and X-ray photoelectron spectroscopy (XPS) [16] revealed that atoms in a molecule interact with the local chemical environment, leading, in turn, to changes in the electron distributions. Thus the probability of a positron annihilating with electrons at specific locations in the molecule are expected, in general, to be different. One might compare, for example, annihilation on the fluorine atoms and the C-H bonds in partially fluorinated benzenes, to gain further insights of the interaction of low-energy positrons with atoms and molecules [3]. As a result, the bound electron wave functions in molecules, which are directly associated with chemical bonding, can play an important role in accurately determining annihilation rates and  $\gamma$ -ray Doppler shift spectra of molecules<sup>1</sup> [1,2,10,23]. In the present study, the low energy plane wave positron (LEPWP) that we recently developed<sup>1</sup> [2,10,23] is employed to investigate the chemical effects of the bound electrons on the  $\gamma$ -ray annihilation spectra of fluorobenzene molecules, focusing, in particular, on the charge distributions and aromaticity.

It is important to note that the absolute values of the positron annihilation rates (or normalized rates,  $Z_{eff}$ ) are very sensitive to the details of the positron-molecule interaction. In particular, they can be strongly enhanced due to positron capture in vibrational Feshbach resonances and intramolecular vibrational energy redistribution, which increase the time the positron spends at the molecule [1]. Understanding these rates is a problem in its own right and the subject of active research. In this paper we focus on a different problem of the *shapes* of the  $\gamma$ -ray annihilation

spectra, which are largely determined by the electron momentum distributions in the molecules.

## 2 Methods and computational details

The  $\gamma$ -ray spectrum of positron annihilation with a many-electron target is determined by the two-photon momentum density function (see, e.g., Ref. [11])

$$W_f(\mathbf{P}) = |A_{i\mathbf{k}}(\mathbf{P})|^2, \quad (1)$$

where  $A_{i\mathbf{k}}(\mathbf{P})$  is the annihilation amplitude for the positron with momentum  $\mathbf{k}$  and electron in orbital  $i$ , which leaves the positive ion in the final state  $f$ , and  $\mathbf{P}$  is the total momentum of the electron-positron pair which is carried by the annihilation photons. Since the photons are emitted in the frame moving with velocity  $\mathbf{V} = \mathbf{P}/2$  (atomic units, where the electron mass  $m = 1$ , are used), the photon energy is Doppler shifted. The shift of the photon energy from the center of the line ( $E = mc^2$ ) is given by  $\varepsilon = cP \cos\theta/2$ , where  $\theta$  is the angle between the direction of the photon and the velocity of the electron-positron pair. In the independent-particle approximation, the annihilation amplitude is given by [11]

$$A_{i\mathbf{k}}(\mathbf{P}) = \int \psi_i(\mathbf{r})\varphi_{\mathbf{k}}(\mathbf{r})e^{-i\mathbf{P}\cdot\mathbf{r}}d\mathbf{r}, \quad (2)$$

where  $\psi_i(\mathbf{r})$  is the wavefunction of the bound electron in state  $i$ , and  $\varphi_{\mathbf{k}}(\mathbf{r})$  is the positron wavefunction. In the LEPWP approximation, the wavefunction of a positron is approximately unity [2],  $\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ . In this case, averaging over the directions of the photon, and summing over all electron orbitals, the photon Doppler-shift-energy spectrum is given by [2]

$$\begin{aligned} W(\varepsilon) &= \frac{1}{c} \sum_f \int \int_{2|\varepsilon|/c}^{\infty} W_f(\mathbf{P}) \frac{PdPd\Omega_P}{(2\pi)^3} \\ &= \frac{1}{c} \int_{2|\varepsilon|/c}^{\infty} \sigma_{EMS}^{total}(P)(PdP), \end{aligned} \quad (3)$$

where  $\sigma_{EMS}^{total}(P)$  is the total electron momentum density. The annihilation line-shape parameter, namely, the full width at half maximum (FWHM) or the  $\gamma$ -ray Doppler-shift spectrum can be obtained using equation (3). In the LEPWP approximation [2], the annihilation spectra are determined by the momentum distributions of the bound electrons of the target<sup>1</sup> [2,10,23].

The numerical accuracy of the LEPWP model will depend on the inclusion of the density produced by the wavefunction, which can be measured by the electron (density) loss of the model. The electron loss can be calculated by the difference between the total number of electrons in the molecule,  $Z$ , and the calculated  $Z_{cal}$ . The latter,  $Z_{cal}$ , in the independent particle approximation is given by [11]

$$Z_{cal} = \int w(\varepsilon)d\varepsilon = \sum_f \int A_{i\mathbf{k}}(\mathbf{P}) \frac{d^3P}{(2\pi)^3}. \quad (4)$$

In the LEPWP approximation this quantity is simply equal to the number of target electrons [2] in theory. The magnitudes of the measured  $Z_{eff}$  for the fluorobenzenes are dominated by the Feshbach resonance processes [1,24], so that will not come out of our present theoretical approach.

Electron wavefunctions of the bound electrons of the fluorobenzene molecules are calculated quantum mechanically, using the density functional theory (DFT) based B3LYP/TZVP model. This is the same model employed in our previous studies<sup>1</sup> [2,10,23] for comparison purposes. The basis set employed is the density-functional triple zeta with valence polarised orbitals (TZVP) [25]. This scheme is found to produce good agreement with the experimental results for the molecular properties, and it is also a sufficiently small basis set to be able to apply to relatively large molecules [26].

The Hirshfeld scheme evaluates a point charge condensed on the  $k$ th atom in a molecule as [27,28]

$$Q_A^H = Z_A - \int \frac{\rho_A(\mathbf{r})}{\rho_{pro}(\mathbf{r})} \rho_{mol}(\mathbf{r}) d^3\mathbf{r}, \quad (5)$$

where  $Z_A$  is the nuclear charge, and  $\rho_A(\mathbf{r})$  is the spherically-averaged atomic electron density centred on nucleus A. And the  $\rho_{pro}$  and  $\rho_{mol}$  are the sums of electron density over the atoms belonging to the promolecule and molecule respectively. A promolecule is defined to be a model of a molecule where the electron density distributions of each of its atoms have been spherically averaged and placed at their minimum energy positions [29]. The Hirshfeld charge predicts site selectivity (e.g., reactive sites) that agrees well with experiment in most cases [28]. It is, for example, generally superior to other schemes such as the Mulliken and natural population analyses [30]. As a result, the Hirshfeld charge scheme is employed in the present study.

### 3 Results and discussion

There are a total of 12 possible fluorinated benzenes with one to six fluorine substitutions of the hydrogen atoms on the benzene ring. Figure 1 gives the chemical structures and the related total electron energies of the fluorobenzenes ( $C_6H_{6-n}F_n$ ,  $n = 0, 1, \dots, 6$ ) calculated using the B3LYP/TZVP model. The fluorinated benzenes are all planar and possess one of five point group symmetries, depending on the number of fluorine atoms present and their positions in the ring:  $D_{6h}$ ,  $D_{3h}$ ,  $D_{2h}$ ,  $C_{2v}$ , and  $C_s$ . The substituted benzenes undergo distortions from the  $D_{6h}$  symmetry to yield a reduced point group symmetry, in order to stabilize the structures of the derivatives. These lower symmetry structures exhibit the Jahn-Teller effect [31]. The unsubstituted benzene ( $C_6H_6$ ) and the fully substituted benzene ( $C_6F_6$ ) both possess  $D_{6h}$  point group symmetry. In Figure 1, the total electronic energies do not seem to be correlated with the symmetry of the structures in the cases where more than one isomer is present. The lowest energy structures

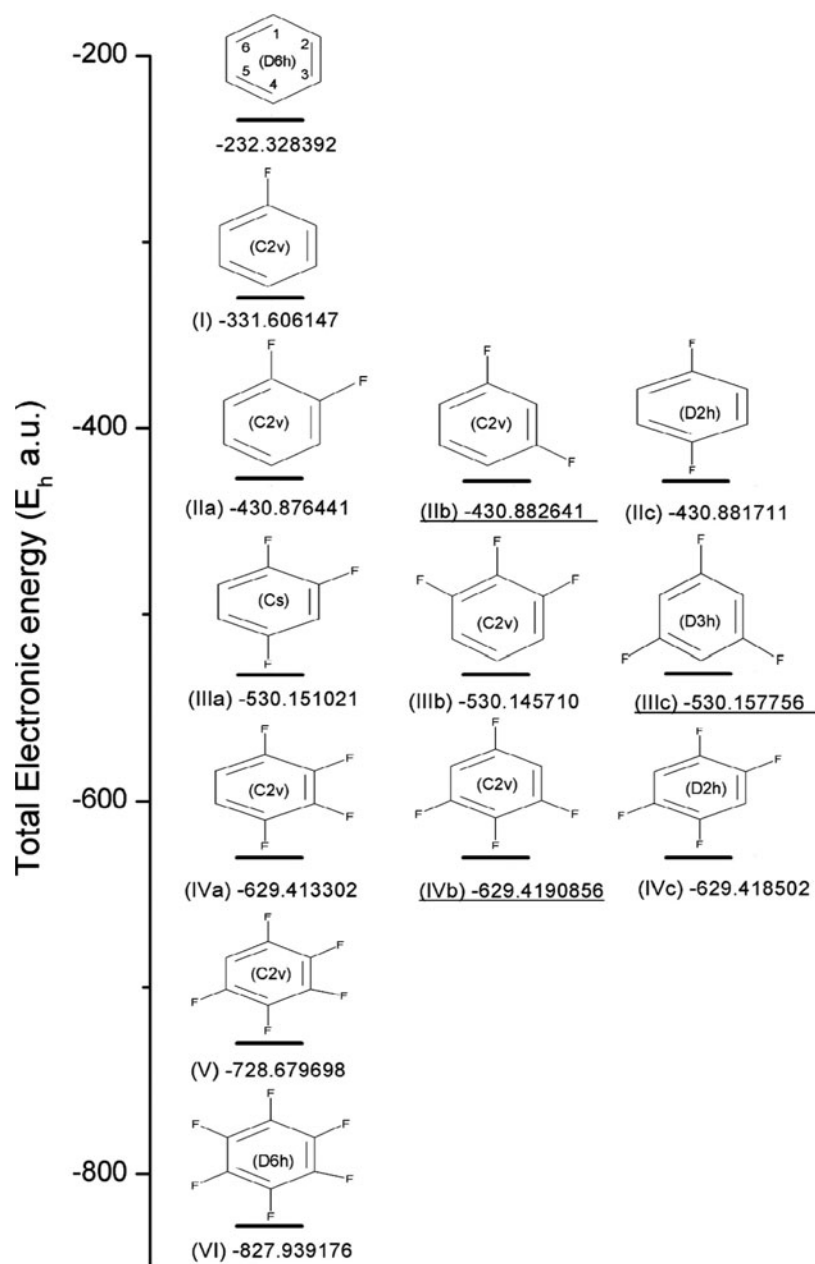
among the isomers are underlined in the figure. For example, of the three difluorinated species, 1,3-difluorobenzene (meta-, IIb) yields the lowest energy and possesses a  $C_{2v}$  point group symmetry. However, in the trifluorinated benzenes, 1,3,5-trifluorobenzene (IIIc) is the lowest energy structure and has  $D_{3h}$  symmetry.

From the data in Table 1S (in the supplementary materials), it is apparent that fluorine substitution in benzene affects the bond lengths within the ring. Fluorine substitution slightly reduces the ring perimeter,  $R_6$  [32] (from 0.01 to 0.03 Å) with the unsubstituted benzene being the largest ( $R_6 = 8.35$  Å [33]). Here the ring perimeter,  $R_n$ , is defined as the sum of the bond lengths formed by the  $n$ -atoms forming the ring [32]. The C-C bond length shortens as the fluorine atoms bond with the carbon atoms: the C-C bond length is 1.392 Å in unsubstituted benzene but 1.384 Å in single-fluorine benzene (I). Regarding the C-F bonds, their lengths reduce gradually from 1.355 Å (I) to 1.333 Å (VI) when the number of fluorine atoms increases.

Molecular properties of the fluorobenzenes, such as the permanent dipole moment and aromaticity, are important features of aromatic compounds. For example, previous studies [13] have indicated certain correlation between positron-molecule binding energies and their dipole moments. Fluorobenzenes are aromatic compounds for which aromaticity accounts for the additional structural stability and chemical reactivity. Although the most appropriate criterion for determining aromaticity is still subject to debate, one of the most widely used indices is the nucleus independent chemical shift (NICS) [34]. Various comparative studies of the aromaticities of perfluorinated benzenes have been reported [35–37]. The NICS<sub>max</sub> index [38], which is a recently introduced aromaticity indicator, is employed in the present study in order to assess the aromatic nature of the fluorinated benzenes.

Table 1 reports the calculated dipole moment and the aromaticity NICS<sub>max</sub> index [38] of the fluorobenzenes. As can be seen in this table, the totally symmetric compounds do not possess a permanent dipole moment. For example, compounds such as  $C_6H_6$ , 1,4- $C_6H_4F_2$  (IIc), 1,3, 5- $C_6H_2F_4$  (IIIc), 1,2, 4,5- $C_6H_2F_4$  (IVc) and  $C_6F_6$  do not have a permanent dipole, whereas 1,2,3- $C_6H_3F_3$  (IIIb) possesses the largest dipole moment among the fluorobenzenes of 3.15 Debye. The aromaticity NICS<sub>max</sub> index, in general, increases as the number of fluorine atoms increases, though it varies among the isomers. For example, benzene exhibits the smallest NICS<sub>max</sub> index as 6.029 whereas it is 9.704 for perfluorobenzene.

Systematically calculated theoretical linewidths (FWHM or  $\Delta\varepsilon$ ) (i.e., the Doppler shift spectral widths for benzene and fluorinated benzenes,  $C_6H_{6-n}F_n$ ,  $n = 0, 1, \dots, 6$ ) based on the LEPWP approximation, are given in Table 2, together with available experimental data. When comparing benzene  $C_6H_6$  and perfluorobenzene  $C_6F_6$ , the unsubstituted benzene  $C_6H_6$  yields the smallest  $\Delta\varepsilon$ , at 2.23 keV [3]. The Doppler shift,  $\Delta\varepsilon$ , increases as more fluorine atoms are substituted into the benzene ring (i.e., as the number of fluorine,  $n$ , increases) [3]. For example, the experimentally measured



**Fig. 1.** Structures of the molecules, the notations in brackets represent the corresponding perfluorinated benzenes as shown in Table 1.

widths are 2.43, 2.66, 2.71, 2.77, 2.89 and 2.95 keV for C<sub>6</sub>H<sub>5</sub>F, C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, C<sub>6</sub>H<sub>3</sub>F<sub>3</sub>, C<sub>6</sub>H<sub>2</sub>F<sub>4</sub>, C<sub>6</sub>H<sub>1</sub>F<sub>5</sub> and C<sub>6</sub>F<sub>6</sub>, respectively. The same trend is observed in the  $\Delta\varepsilon$  values calculated using the LEPWP approximation (Tab. 2). It should also be noted that, while the absolute discrepancy,  $\Delta = \Delta\varepsilon(\text{calc.}) - \Delta\varepsilon(\text{expt.})$ , increases as the molecular size increases, the relative discrepancy,  $\Delta/\Delta\varepsilon(\text{calc.})$ , remains almost unchanged at 30–33%. This is consistent with the result found previously for atoms and small molecules<sup>1</sup> [2,10,23].

The main reason for this discrepancy, as pointed out by Green et al. [10], is the neglect of the positron repulsion from the nuclei, leading to an overestimate of the

contribution of small positron-nuclear separations where the electron momentum is large [10]. The large differences between  $\Delta\varepsilon(\text{core})$  and  $\Delta\varepsilon(\text{total})$  shown in Table 2 indicate that the core-electron contribution to the  $\gamma$ -ray spectra is small. This is in agreement with previous findings that the contributions from the inner shells are very small, namely only a few percent for noble gases and small molecules<sup>1</sup> [2,10,23]. It is the valence electrons [2] whose contributions dominate the annihilation process and, therefore, the Doppler shift spectra.

Figure 2 compares the calculated FWHM ( $\Delta\varepsilon$ ) of the positron annihilation spectra of: (a) valence electrons, and (b) total electrons with experimental data.

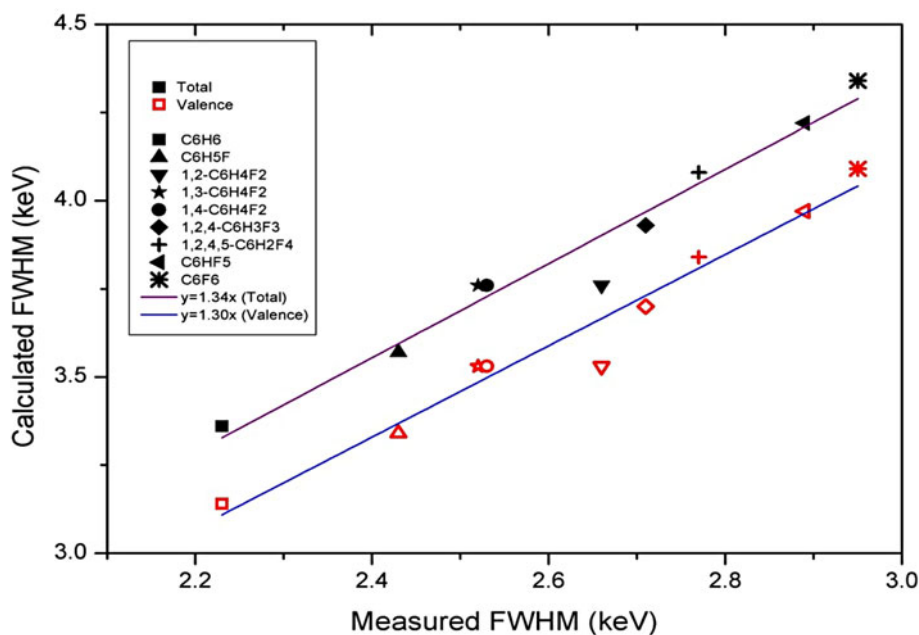
**Table 1.** Calculated molecular properties of fluorinated benzenes.

Molecule		B3LYP/TZVP				Expt. [35]	NICS <sub>max</sub>	OVGF (IP, eV)
		$\mu_x$	$\mu_y$	$\mu_z$	$\mu_{tot}$			
C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>6</sub>	0.00	0.00	0.00	0.00	0.00	6.03	9.09
C <sub>6</sub> H <sub>5</sub> F	I	0.00	0.00	-1.69	1.69	1.60	6.26	9.14
1,2-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	IIa	0.00	0.00	2.79	2.79	2.46	6.80	9.30
1,3-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	IIb	0.00	0.00	1.66	1.66	1.51	6.65	9.35
1,4-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	IIc	0.00	0.00	0.00	0.00	0.00	6.62	9.19
1,2,4-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	IIIa	-0.02	-1.57	0.00	1.57	—	7.14	9.23
1,2,3-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	IIIb	0.00	0.00	-3.15	3.15	1.39	7.27	9.63
1,3,5-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	IIIc	0.00	0.00	0.00	0.00	0.00	6.89	9.71
1,2,3,4-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	IVa	0.00	0.00	-2.66	2.66	—	8.01	9.48
1,3,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	IVb	0.00	0.00	1.49	1.49	—	7.77	9.49
1,2,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	IVc	0.00	0.00	0.00	0.00	0.00	7.92	9.33
C <sub>6</sub> HF <sub>5</sub>	V	0.00	0.00	-1.49	1.49	1.44	8.78	9.62
C <sub>6</sub> F <sub>6</sub>	VI	0.00	0.00	0.00	0.00	0.00	9.70	9.90

**Table 2.** FWHM  $\Delta\epsilon$  of the annihilation spectra for fluorinated benzenes based on B3LYP/TZVP model.

Molecules		$\Delta\epsilon$ (keV)			Effective number of electrons				$\langle R \rangle$ (a.u.)
		Present	Expt. [3]	$\Delta$	Z <sub>cal</sub>	Z	$\Delta$	Expt. [4]	
C <sub>6</sub> H <sub>6</sub>	Core	10.17	—	—	11.34	12	0.66	—	—
	Valence	3.14	—	—	29.97	30	0.03	—	—
	Total	3.36	2.23	1.13	41.31	42	0.69	20300	457.89
C <sub>6</sub> H <sub>5</sub> F (I)	Core	10.51	—	—	12.94	14	1.06	—	—
	Valence	3.34	—	—	35.93	36	0.07	—	—
	Total	3.57	2.43	1.14	48.87	50	1.13	45100	649.44
1,2-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> (IIa)	Core	10.81	—	—	14.54	16	1.46	—	—
	Valence	3.53	—	—	41.88	42	0.12	—	—
	Total	3.76	2.66	1.1	56.43	58	1.57	32800	821.32
1,3-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> (IIb)	Core	10.80	—	—	14.54	16	1.46	—	—
	Valence	3.53	—	—	41.88	42	0.12	—	—
	Total	3.76	2.52	1.24	56.43	58	1.57	13100	879.93
1,4-C <sub>6</sub> H <sub>4</sub> F <sub>2</sub> (IIc)	Core	10.81	—	—	14.54	16	1.46	—	—
	Valence	3.53	—	—	41.88	42	0.12	—	—
	Total	3.76	2.53	1.23	56.43	58	1.57	13500	911.78
1,2,4-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub> (IIIa)	Core	11.07	—	—	16.15	18	1.85	—	—
	Valence	3.70	—	—	47.84	48	0.16	—	—
	Total	3.93	2.71	1.22	63.99	66	2.01	10100	1112.73
1,2,6-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub> (IIIb)	Core	11.07	—	—	16.15	18	1.85	—	—
	Valence	3.69	—	—	47.84	48	0.16	—	—
	Total	3.91	—	—	63.99	66	2.01	—	1032.95
1,3,5-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub> (IIIc)	Core	11.07	—	—	16.15	18	1.85	—	—
	Valence	3.69	—	—	47.84	48	0.16	—	—
	Total	3.93	—	—	63.99	66	2.01	—	1134.54
1,2,3,4-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> (IVa)	Core	11.31	—	—	17.75	20	2.25	—	—
	Valence	3.84	—	—	53.80	54	0.20	—	—
	Total	4.08	—	—	71.55	74	2.45	—	1296.68
1,3,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> (IVb)	Core	11.31	—	—	17.75	20	2.25	—	—
	Valence	3.84	—	—	53.80	54	0.20	—	—
	Total	4.08	—	—	71.55	74	2.45	—	1341.51
1,2,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> (IVc)	Core	11.31	—	—	17.75	20	2.25	—	—
	Valence	3.84	—	—	53.80	54	0.20	—	—
	Total	4.08	2.77	1.31	71.55	74	2.45	2760	1368.81
C <sub>6</sub> HF <sub>5</sub> (V)	Core	11.52	—	—	19.35	22	2.65	—	—
	Valence	3.97	—	—	59.76	60	0.24	—	—
	Total	4.22	2.89	1.33	79.11	82	2.89	1930	1574.52
C <sub>6</sub> F <sub>6</sub> (VI)	Core	11.70	—	—	20.95	24	3.05	—	—
	Valence	4.09	—	—	65.72	66	0.28	—	—
	Total	4.34	2.95	1.39	86.67	90	3.33	499	1826.22





**Fig. 2.** (Color online) Comparisons of the calculated and experimentally measured FWHM of the positron annihilation spectra of benzene and its fluorinated derivatives. The solid lines show that the calculated values are about 30% and 34% greater than experimental results for valence and total respectively.

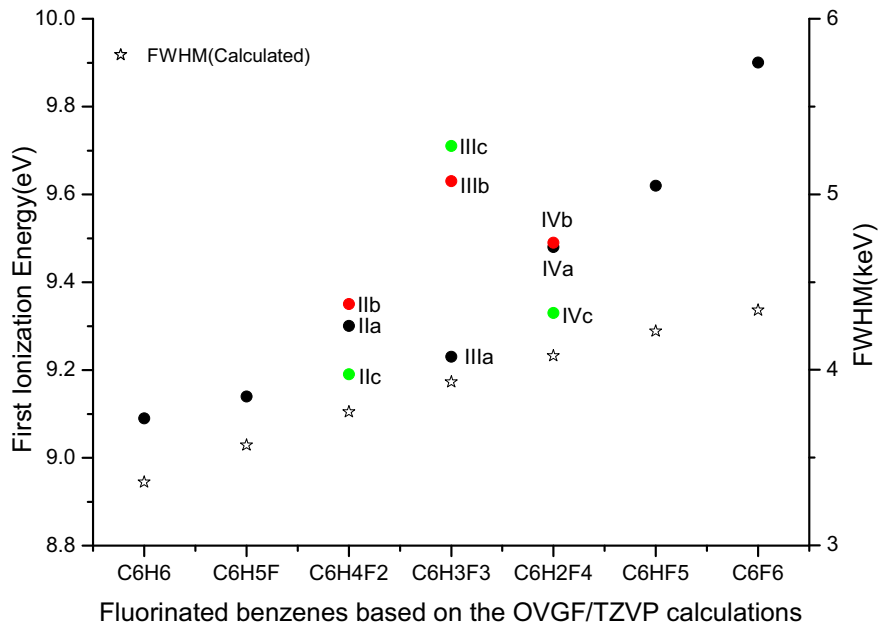
The averaged differences between the calculated  $\Delta\varepsilon(\text{total})$  and  $\Delta\varepsilon(\text{valence})$  of benzene and its fluorinated derivatives are ca. 0.23 keV, with 0.22 keV for benzene and 0.25 keV for  $\text{C}_6\text{F}_6$ . As shown in this figure, one finds that the calculated valence and total spectra are approximately 30% and 34% broader than the measurements respectively. This is in agreement with our previous findings<sup>1</sup> [1,2,10]. The fact that the Doppler shifts due to the valence electrons agree with the measurements better than the total FWHM values (in the LEPWP approximation) in a molecule suggests that the actual  $\gamma$ -ray spectra are not just a simple sum over momentum densities of all electrons in the molecule, and that the annihilation process most likely takes place on valence electrons as found in noble gases [2]. As a result, inclusion of the momentum-dependent correction factors in the calculations is expected to lead to improved agreement with the experimental measurements [10].

The experiments indicate that in halo-hydrocarbon molecules, a positron annihilates with all of the valence electrons in the molecule, including those associated with the halogen atoms, with similar probabilities [3]. In the present study, the contribution of the fluorine atoms to the annihilation spectra is seen clearly since the FWHM ( $\Delta\varepsilon$ ) exhibits a linear relationship with the number of fluorine atoms. In order to obtain additional information regarding the sites of annihilation, the atomic electro-negativity has been calculated for the fluorinated benzenes. Table 3 gives the calculated Hirshfeld charges,  $Q^{\text{H}}$ , calculated based on equation (5), for each atom of the benzene derivatives, with the negative charges being highlighted. The Hirshfeld charges in this table present a certain pattern reflecting the structure and symmetry of the molecules. All the carbon atoms are equivalent in  $\text{C}_6\text{H}_6$  and  $\text{C}_6\text{F}_6$  but with op-

posite charges, whereas the six fluorine (hydrogen) atoms possess negative (positive) charges.

The carbons are negatively charged when bonded to hydrogen atoms, but switch signs when bonding with fluorines. Hydrogen atoms always exhibit positive charges, but are more positively charged (with less electrons) in the fluorinated benzenes than in the benzene. For example, the Hirshfeld charges of the carbon atoms and hydrogen atoms in benzene are  $-0.044$  a.u. and  $0.044$  a.u., respectively. In  $\text{C}_6\text{H}_5\text{F}$ ,  $Q^{\text{H}}$  of the fluorine is  $-0.157$  a.u., whereas C(1) which bonds with the F atom switches sign to become positively charged at  $0.103$  a.u. Other carbon atoms in the molecule retain negative charges with charge redistribution, depending on the new symmetry; so do the positive charges of the hydrogen atoms in  $\text{C}_6\text{H}_5\text{F}$ . Apparently, when the hydrogen atoms are substituted by an equal number of fluorine atoms, the electronegative fluorine atom induces charges on the atoms in a compound and so further polarizes the bonds around it. That is, both hydrogen and carbon atoms play a role as electron donors, whereas fluorine atoms are electron acceptors.

The result of an annihilation process in a molecule is that a molecular ion is produced with one less electron (i.e., the molecule is ionized). There may be certain correlations between the ionization energies of a molecule and the  $\gamma$ -ray Doppler shift spectra. In order to explore such correlation, Figure 3 presents the calculated first ionization potentials (IPs) of the fluorobenzenes using the outer valence Green function (OVGF) model and their FWHM Doppler shifts using the B3LYP/TZVP model. This figure indicates that there is indeed a positive correlation between the first IPs and the Doppler shifts: the larger the first IP, the larger the Doppler shift.



**Fig. 3.** (Color online) Correlation between IPs and  $\Delta\varepsilon$  for benzene and fluorobenzenes.

**Table 3.** (Color online) Hirshfeld charges ( $Q_A^H$ ) of the fluorobenzene derivatives.

Site	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>5</sub> F	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	C <sub>6</sub> HF <sub>5</sub>	C <sub>6</sub> F <sub>6</sub>
		I	IIa	IIb	IIc	IIIa	IIIb	IIIc	IVa	IVb	IVc	V	
C(1)	-0.044	0.103	0.100	0.110	0.103	0.1	0.098	0.117	0.104	0.116	0.107	0.111	0.107
C(2)	-0.044	-0.047	0.100	-0.051	-0.039	0.108	0.106	-0.052	0.103	-0.046	0.107	0.101	0.107
C(3)	-0.044	-0.036	-0.041	0.110	-0.039	-0.044	-0.042	0.117	0.103	0.113	-0.038	0.109	0.107
C(4)	-0.044	-0.045	-0.037	-0.048	0.103	0.110	-0.029	-0.052	0.104	0.096	0.107	0.101	0.107
C(5)	-0.044	-0.036	-0.037	-0.028	-0.039	-0.04	-0.042	0.117	-0.035	0.113	0.107	0.111	0.107
C(6)	-0.044	-0.047	-0.041	-0.048	-0.039	-0.033	0.106	-0.052	-0.035	-0.046	-0.038	-0.04	0.107
F(1)	-	-0.157	-0.140	-0.148	-0.153	-0.137	-0.123	-0.139	-0.129	-0.137	-0.129	-0.122	-0.107
F(2)	-	-	-0.140	-	-	-0.132	-0.132	-	-0.116	-	-0.129	-0.114	-0.107
F(3)	-	-	-	-0.148	-	-	-	-0.139	-0.116	-0.124	-	-0.109	-0.107
F(4)	-	-	-	-	-0.153	-0.145	-	-	-0.129	-0.121	-0.129	-0.114	-0.107
F(5)	-	-	-	-	-	-	-	-0.139	-	-0.124	-0.129	-0.122	-0.107
F(6)	-	-	-	-	-	-	-0.132	-	-	-	-	-	-0.107
H(1)	0.044	-	-	-	-	-	-	-	-	-	-	-	-
H(2)	0.044	0.058	-	0.072	0.064	-	-	0.075	-	0.080	-	-	-
H(3)	0.044	0.050	0.064	-	0.064	0.077	0.066	-	-	-	0.083	-	-
H(4)	0.044	0.047	0.053	0.061	-	-	0.059	0.075	-	-	-	-	-
H(5)	0.044	0.050	0.053	0.056	0.064	0.066	0.066	-	0.072	-	-	-	-
H(6)	0.044	0.058	0.064	0.061	0.064	0.069	-	0.075	0.072	0.080	0.083	0.085	-

Unlike atomic systems, even small molecules are significantly more complicated than atoms, as molecules possess multiple centers and involve interactions among the component atoms<sup>1</sup>. Larger molecules exhibit significantly different chemical environments that contribute to the  $\gamma$ -ray spectra, as observed by the Surko group [8,9]. However, the present calculations indicate that the FWHM Doppler shifts ( $\Delta\varepsilon$ ) of the  $\gamma$ -ray spectra are more sensitive to the number of total (valence) electrons in the molecule, rather than their chemical environment. This is in contrast to their annihilation rates,  $Z_{eff}$ . The present theory predicts that all isomers possess almost the same

Doppler shifts, and so it is not possible to differentiate isomers of the same chemical composition from the molecular annihilation Doppler spectra, as shown in Table 2. However, the present numerical method based on spherically averaged momentum distribution (i.e., Eq. (3)) may cause the loss of useful angular dependent chemical information. For example, the calculated  $\Delta\varepsilon$  of the fluorinate benzene isomers, 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 1,3-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and 1,4-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, are all the same at 3.53 keV for valence electrons and 3.76 keV for all electrons, whereas the measured  $\Delta\varepsilon$ 's are given by 2.66, 2.52 and 2.53 keV, respectively. This may be due to the spherically average in their total momenta in equation (3),

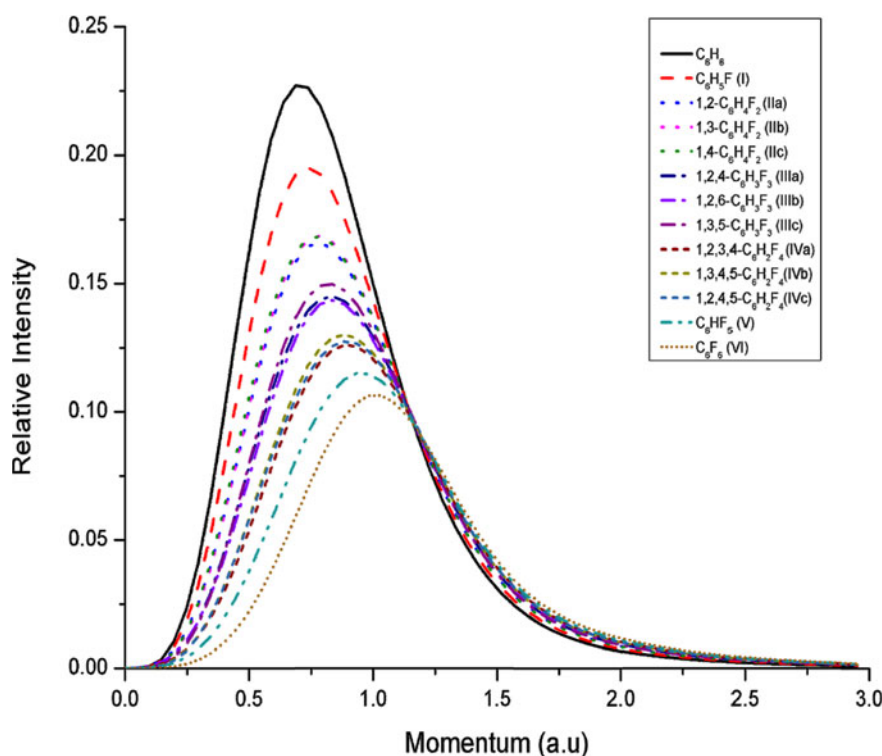


Fig. 4. (Color online) Total momentum distributions of the fluorobenzenes.

causing molecule specific information loss. Figure 4 reports the total momentum distributions of the fluorinated benzenes, whereas the supplementary information in Figure 1S gives the momentum distributions of individual valence orbitals of difluorobenzenes. As can be seen in Figure 4, the total momentum distributions of a molecule is almost always a bell shape, whereas their individual orbital momentum distributions are orbital specific and can possess several maxima, as shown in Figure 1S.

The measured  $Z_{eff}$  values of the fluorobenzenes differ dramatically. Instead of showing a linear increase with the number of fluorine atoms, as does the FWHM Doppler shift, the measured  $Z_{eff}$  peaks at 45 100 for  $C_6H_5F$  before it drops until it reaches the minimum at  $Z_{eff} = 499$  of the fully substituted  $C_6F_6$ . There are also interesting differences in the measured  $Z_{eff}$  values for the isomers of  $C_6H_4F_2$ , IIa, IIb and IIc, which are equal to 32 800, 13 100 and 13 500, respectively. These isomers only differ by the relative locations of the two fluorine atoms. Hence, this suggests that the  $Z_{eff}$  (i.e., the absolute magnitudes of the  $\gamma$ -ray spectra) is a property which is sensitive to the chemical structure of the molecules, rather than simply the number of electrons in a molecule. This is believed to be due to the vibrational resonant attachment of the positron to these species [1,12,24].

In the numerical scheme used in the present study, a momentum cut-off of the integrals in equations (3) and (4) was taken to be 10 a.u. As discussed previously<sup>1</sup>, this cut-off is insufficient for the core orbitals and results in noticeable loss in core electron momentum density of the target. This loss increases as the number of more strongly

bound core orbitals (i.e., the 1s of fluorine atoms) increases. Table 2 shows the loss of electron density in the calculations based on the numerical cut-off at momentum  $p = 10$  a.u. [2]. As expected, the electron density loss is more significant in core shell than in valence shell. When the molecule contains more fluorine atoms, the core electron density loss becomes larger. For example, for  $C_6H_5F$ , the electron density loss is 1.06 (i.e., 7.57%) and 0.07 (i.e., 0.19%) in core and valence shells, respectively. However, the core electron density losses in benzene ( $C_6H_6$ ) and fully fluorinate benzene ( $C_6F_6$ ) are 5.5% and 12.7%, respectively. Since the valence orbitals dominate the annihilation processes, the impact of the cut-off in this numerical scheme on the FWHM values can be relatively small.

## 4 Concluding remarks

Using the low energy plane wave positron (LEPWP) approximation, the positron-electron annihilation  $\gamma$ -ray Doppler shift spectra in benzene and fluorinated benzenes have been simulated using the robust modern computational chemistry B3LYP/TZVP model. The present study confirms that the LEPWP approximation yields a  $\sim 30\%$  overestimate of the measured Doppler shifts for this group of aromatic molecules. This result is in agreement with our previous experiences with noble gases [2] and small molecules<sup>1</sup> [10]. The present study further reveals that the Doppler shift is proportional to the number of molecular electrons and the aromaticity of the molecule, but less sensitive to the isomeric chemical environment.



Substitution of fluorine atoms into the benzene ring polarizes the chemical bonds of the resulting derivatives and causes redistribution of the electron charge density. The presence of fluorine atoms lead to electron density being removed from the carbon atoms so that the sign of charge on the carbons switches sign to positive. This electron density and that donated from other C-H bonds in the compounds then reside on the fluorines. As a result, the fluorine atoms may become even more dominant annihilation sites in the compounds, which are suggested by the calculated atomic site Hirshfeld charges and two-dimensional molecular electrostatic potentials of the compounds.

It is also confirmed that the valence electrons dominate the annihilation spectra. However, it is unclear how sensitive the Doppler shift ( $\Delta\varepsilon$ ) is to the chemical structures of isomers. In particular, the calculations report the same  $\Delta\varepsilon$  for the isomers, which is contrary to some experimental data. However, the differences in  $\Delta\varepsilon$  among the measured three isomers, 1,2-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, 1,3-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> and 1,4-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub>, are small, and no other isomer measurements are available. This is a current limitation in the study of sensitivity in  $\Delta\varepsilon$  to these changes in chemical structure. On the other hand, identical results for the same isomers from theory may be due to application of the spherically averaged total momentum distributions (i.e., Eq. (3)) which can lead to a loss of orbital-specific information of the compounds. This electron orbital anisotropy can be enhanced if a realistic positron wavefunction which reflects the charge distribution in the molecule (rather than constant) is used.

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