

Gamma-ray spectra from low-energy positron annihilation processes in molecules

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The theoretical γ -ray spectra from positron-electron annihilation process in a wide variety of atoms and molecules are studied. The theoretical Doppler broadened γ -ray spectra for core, inner valence, and outer valence electrons of these molecules are studied systematically. The present results show that the experimental γ -ray spectra agree well with inner valence electrons, especially the lowest occupied valence orbital electrons rather than the outer valence electrons. These inner valence electrons show a strong correlation with the corresponding available experimental measurements. These findings are interesting because the outer valence electrons have been supposed to have larger probability annihilating with positrons rather than the inner valence electrons. The present work also suggests that the accurate positron wave functions must be involved to identify the dominance of the bound electrons clearly in positron-electron annihilation process.

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I. INTRODUCTION

The interaction of low-energy positrons with atoms and molecules is an active research field in numerous subjects, such as scattering [1,2], positronium formation [3], and positron annihilation [4–8]. The theoretical [9,10] and experimental [11–14] studies show that the electron correlation [15–17], molecular vibrations [19,20], even atomic excited states [21] and the positron wave function in atoms or molecules must be considered to get agreeable results. However, even for atoms, it is hard to get the accurate positron wave function due to little knowledge about what happened and how at the annihilating moment. Recently, the Doppler-broadened γ -ray spectra for low-energy positron annihilation in many gas-phase molecules have been measured extensively with milestone achievements [4,7,18]. The theoretical predicted profiles of the γ -ray for most of molecules are only within about 70% agreement with the experiments [9,10,15,16]. In recent years, we studied the contributions of different kinds of bound electrons to the positron annihilation process for some molecules [8,22–29] for which the γ -ray spectra are measured [12]. The annihilation spectra obtained in the recent low-energy plane-wave approximation are always broader than those measured experimentally [7,12] and the inner valence electrons or the outermost s -atomic electrons show strong correlation with the experimental results. These significant theoretical and experimental studies have improved our understanding of the interaction process of positrons with atoms and small molecules. However, most of the measurements have no theoretical spectra, even in relatively simple targets. The understanding of positrons and their behavior in molecules is still incomplete compared to more familiar electron problems. More systematic theoretical calculations are needed to compare with these experimental achievements.

Although the momentum distribution of electrons would be suppressed if a proper positron wave function were used [12], the accurate positron wave function in the annihilation process is still difficult to obtain in the molecular systems. Hence,

theoretical development of the annihilation processes for larger polyatomic molecular systems becomes paramount important even under low-energy positron approximation before the positron wave function is considered. The recent gas-phase measurement [12] provides an excellent opportunity for a more detailed theoretical study of γ -ray spectra of a large number of molecules. The low-energy plane-wave positron approximation to estimate the Doppler-shift spectra of annihilation γ -rays has been developed and tested for noble gas atoms and small molecules in recent work [23–27]. It was theoretically revealed that, the same as the chemical processes, the valence electrons predominantly influence the annihilation process. However, the Doppler shifts of the γ -ray spectra are related mostly with the momentum distribution in the small momentum region. That is, the electrons distributed in the lower momentum region play an important role in the annihilation process. The previous studies of atoms and molecules [22–28] have shown that the inner valence electrons achieve an excellent correlation with the experimental measurements rather than outer valence electrons. This interesting phenomenon attracts us to find out whether molecules have the same roles in general.

The aims of the present study are to investigate the contributions of the individual electrons of the atoms or molecules to the γ -ray spectra. The present study suggests an annihilation model and applies it to calculate the γ -ray positron-electron annihilation spectra for several molecules. Theoretical expressions of the γ -ray spectra in the positron-electron annihilation process are given in Sec. II. The γ -ray spectra for 59 molecules are compared with available measurements to validate the theoretical model and the γ ray for five molecules are predicted in Sec. III. Finally, the conclusions are in Sec. IV.

II. THEORETICAL TREATMENTS AND IMPLEMENTATIONS

The γ -ray spectra are usually measured from the momentum distribution of annihilating electron-positron pairs [10]

$$A_{i\vec{k}}(\vec{P}) = \int \psi_i(\vec{r}) \phi_{\vec{k}}(\vec{r}) e^{-i\vec{P}\cdot\vec{r}} d\vec{r}, \quad (1)$$

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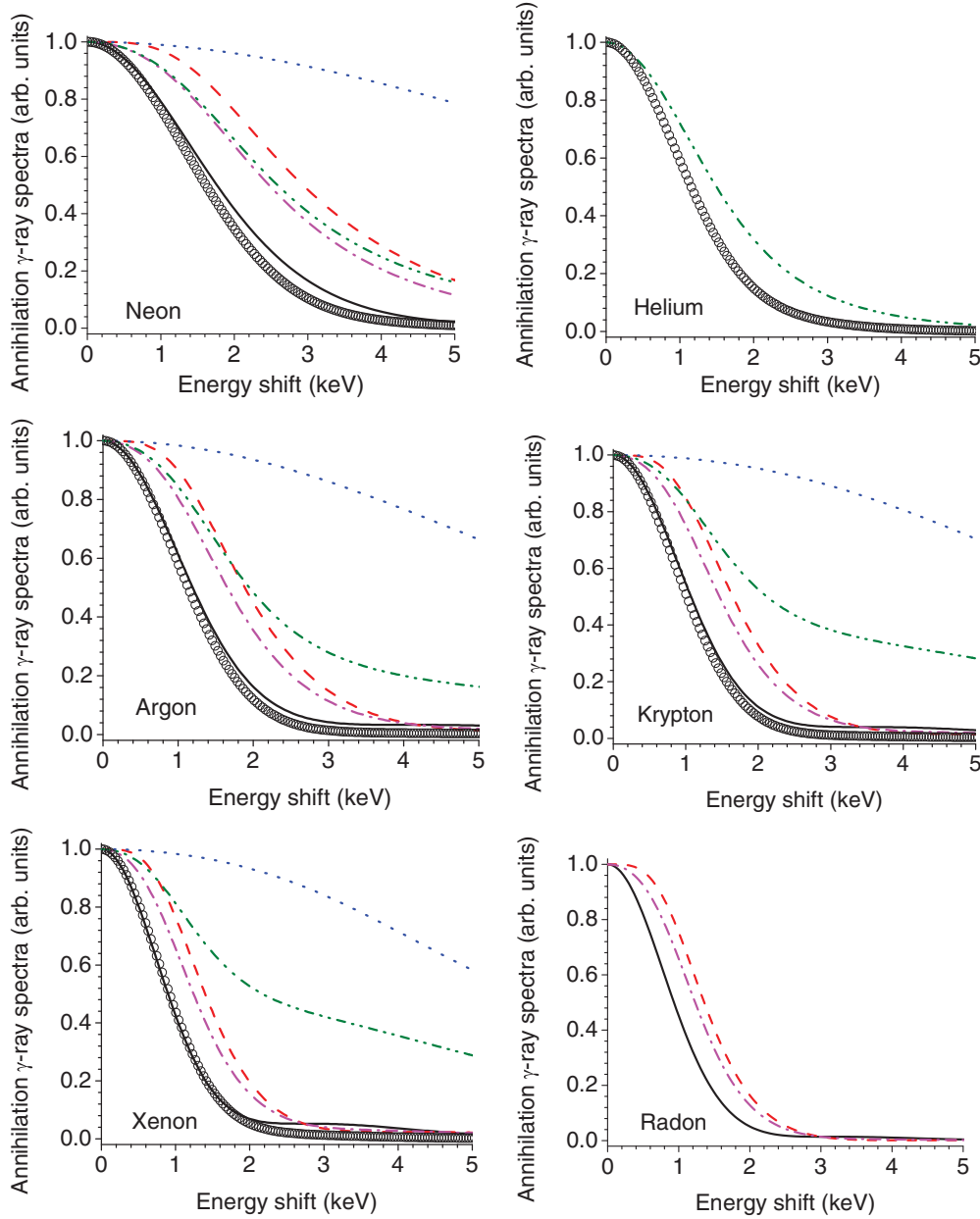


FIG. 1. Comparison of the theoretical γ -ray spectral profiles (lines) of He, Ne, Ar, Kr, Xe in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12]. The profile for noble gas atom Rn is also predicted about 1.94 keV.

where $\phi_{\vec{k}}(\vec{r})$ and $\psi_i(\vec{r})$ are the positron and electron wave function respectively. The positron and electron annihilate at the position \vec{r} and release photons with total momentum \vec{P} . Usually the momentum of positron is significantly smaller than most of the bound electrons, hence the positron wave function can be taken as a small plane wave and neglected in the calculation of the γ -ray spectra for low-energy region [22–28].

In the recent extensive experimental measurements [12], the momentum measurements are performed in gaseous targets. The momentum of the electron-positron pair is rotationally averaged in the gas or liquid experiments. Hence, in order to compare with these experimental measurements, the present theoretical momentum distribution must be spherically averaged. To perform the spherical average, the radial distribution function of positron-electron pairs in momentum space is

defined by [23]

$$D_i(P) = \int_0^\pi d\theta \int_0^{2\pi} d\phi P^2 \sin\theta |A_i(\vec{P})|^2, \quad (2)$$

where P, θ, ϕ are spherical coordinates respectively. Hence, the theoretical spherically averaged momentum distribution is given by [23]

$$\sigma_i(P) = \frac{D_i(P)}{4\pi P^2}. \quad (3)$$

Equation (3) means the averaged probability to encounter the electron-positron pair on the momentum surface with the momentum $|P|$. In the present theoretical calculations, the spherically averaged momentum distribution is used to account

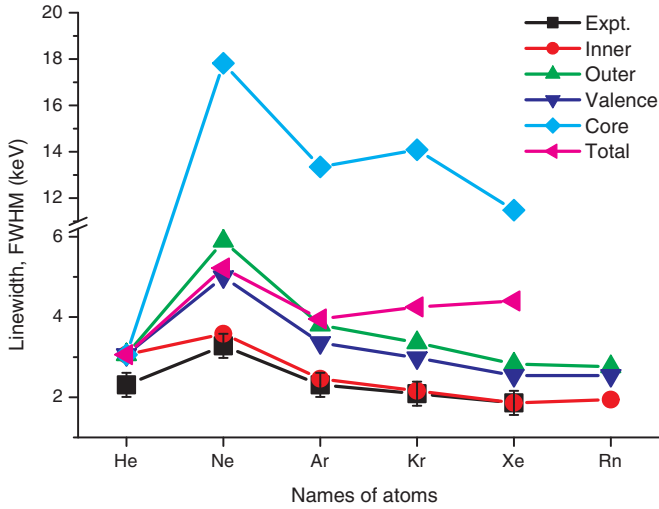


FIG. 2. Comparison of the calculated and experimentally measured FWHM (keV) [12] of γ -ray spectra of noble gas atoms.

for the random orientation effect of gas or liquid molecules in experimental measurements.

The γ -ray in the annihilation process is Doppler shifted in energy due to the longitudinal momentum component of positron-electron pair [7]. Hence, the integration over the plane perpendicular to the P must be performed in order to get the total probability density at the momentum $P = 2\epsilon/c$. Then the γ -ray spectra for electrons of the i th bound orbital annihilating with positrons is given by [23]

$$\Omega_i(\epsilon) = \frac{1}{c} \int_{2\epsilon/c}^{\infty} \sigma_i(P) P dP. \quad (4)$$

The Doppler shift from the center ($mc^2 = 511$ keV) is given by ϵ . Under this theoretical scheme, one can study the γ -ray spectra and compare with the gas experimental measurements.

Most of experiments only give the Doppler shift at full width at half maximum (FWHM) of the γ -ray spectra. In order to compare with the corresponding experimental γ -ray spectra, the FWHM is not enough to identify the γ -ray spectra in the entire energy region $(0, \infty)$. In the present work, in order to find out the correlation between the theoretical prediction and the experimental measurements, the correlation coefficient between the theoretical and the experimental results of the

γ -ray spectra is introduced by

$$\chi(\Omega_T, \Omega_E) = \frac{\sum_{j=1}^N (\Omega_{T,j} - \bar{\Omega}_T)(\Omega_{E,j} - \bar{\Omega}_E)}{\sqrt{\sum_{j=1}^N (\Omega_{T,j} - \bar{\Omega}_T)^2 (\Omega_{E,j} - \bar{\Omega}_E)^2}}, \quad (5)$$

where $\Omega_{E,j}$ and $\bar{\Omega}_E$ are the points in the two-Gaussian fitted experimental γ -ray spectra [12] and the averaged one respectively. While $\Omega_{T,j}$ and $\bar{\Omega}_T$ are the points in the theoretical γ -ray spectra and the averaged one respectively. The number of data N is sufficiently large to represent the γ -ray spectra accurately. In the present study, the correlation coefficient has been used to identify which electron's theoretical spectra have similar behavior with the experimental results. This is helpful to recognize the annihilating electrons in the positron-electron annihilation process, although the correlation coefficient usually overestimates the agreement between two sets of data.

As is well known, the Coulomb interactions and the net charges in molecules play an important role in positron-electron annihilation process [7,9,15,16]. In order to find out the annihilation mechanism in the positron-electron annihilating moment, two factors are used in the analysis of the present theoretical results: a local molecular attraction potential (LMAP) and Hirshfeld charge. In a molecular system, the electrostatic potential (ESP) of a molecule represents the Coulomb interactions with a positive unit charge (a positron exactly). In previous studies, LMAP is introduced to predict the positrophilic or electrophilic site of a molecule [27].

$$U(\vec{r}) = -\rho_p(\vec{r}) \cdot V_{\text{mol}}(\vec{r}). \quad (6)$$

The $\rho_p(\vec{r})$ is the positron density while $V_{\text{mol}}(\vec{r})$ is the total electrostatic potential of a molecule. If $U(\vec{r})$ is positive, this site is attractive to positron and called the positrophilic region in a molecule. Otherwise, if $U(\vec{r})$ is negative, this site is repulsive to positron and called the electrophilic region in a molecule. Obviously, a positron will approach to the positrophilic site to annihilate with an electron in the same region. The total electrostatic potential is defined by

$$V_{\text{mol}}(\vec{r}) = V_{\text{nuc}}(\vec{r}) + V_{\text{ele}}(\vec{r}) = \sum_A \frac{Z_A}{|\vec{r} - \vec{R}_A|} - \int \frac{\rho_e(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}', \quad (7)$$

where Z_A is nuclear charge, \vec{r} and \vec{R}_A are the electrons and the nuclei A coordinates respectively, ρ_e is the electron density. If the positron wave function is a plane wave, the positron density is unity everywhere, the LMAP equals to the negative ESP.

TABLE I. The charge ratio of one positron and the total positive charge in atoms plus one positron. The relative difference of FWHM of inner valence electrons and the experimental results [12].

Molecule (Formula)	Charge ratio	Relative difference with experiments
Helium (He)	$1/(2 + 1) = 33\%$	$(3.06 - 2.31)/2.31 = 33\%$
Neon (Ne)	$1/(10 + 1) = 9\%$	$(3.58 - 3.28)/3.28 = 9\%$
Argon (Ar)	$1/(18 + 1) = 5\%$	$(2.46 - 2.31)/2.31 = 6\%$
Krypton (Kr)	$1/(36 + 1) = 3\%$	$(2.16 - 2.09)/2.09 = 3\%$
Xenon (Xe)	$1/(54 + 1) = 2\%$	$(1.86 - 1.86)/1.86 = 0\%$
Radon (Rn)	$1/(86 + 1) = 1\%$	-

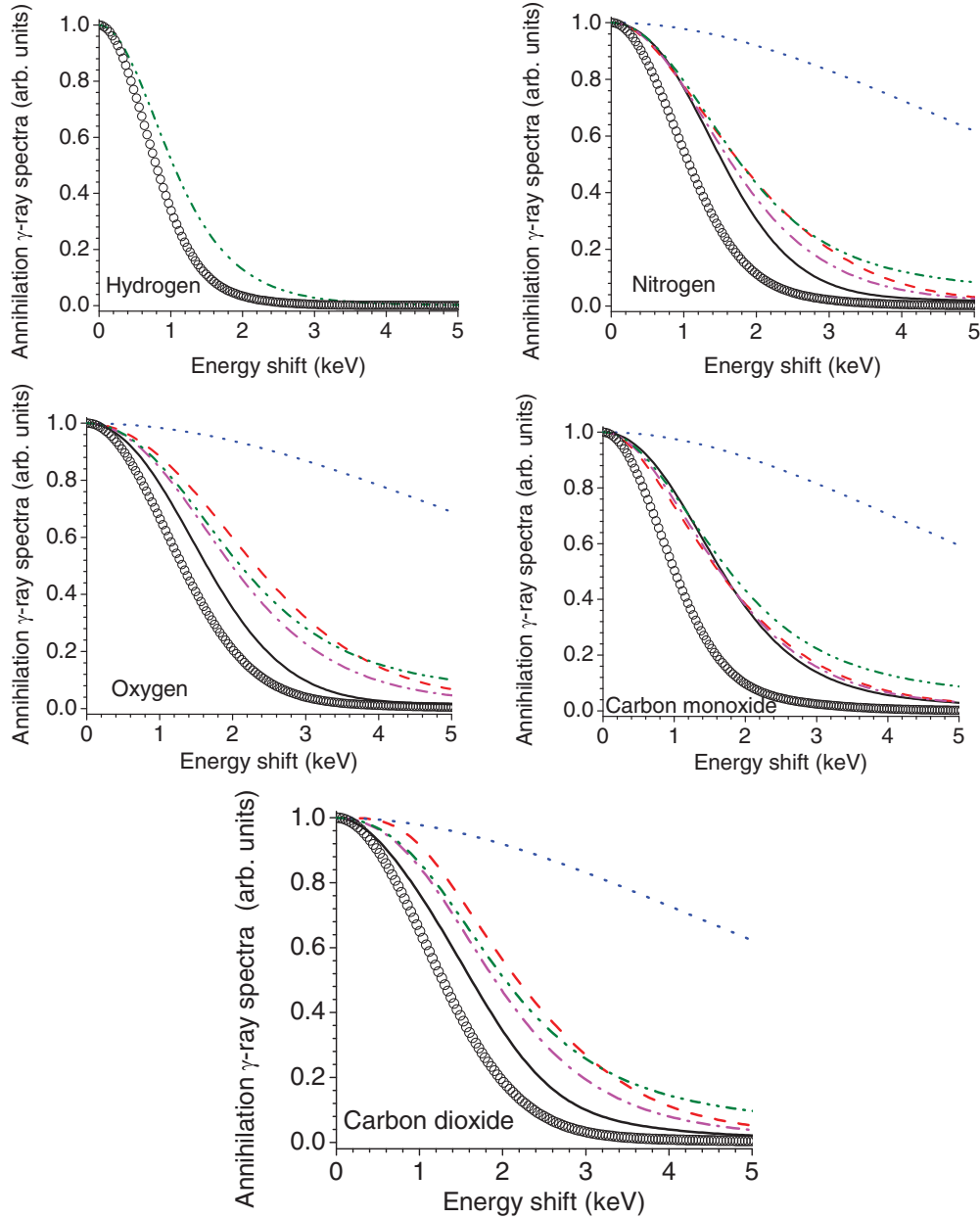


FIG. 3. Comparison of the theoretical γ -ray spectral profiles (lines) of small molecules H_2 , N_2 , O_2 , CO , and CO_2 in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

LMAP indicates the region attracting positrons. However, are there enough net electrons in the positrophilic regions? In order to find where the extra electrons are, we also need the Hirshfeld charge parameters of molecules. The Hirshfeld charge also can be employed to understand the site selectivity and show how many net electrons are in this site. It is defined by

$$Q_A^H = Z_A - \int \frac{\rho_A(\vec{r})\rho_{\text{mol}}(\vec{r})}{\rho_{\text{pro}}(\vec{r})} d^3\vec{r}, \quad (8)$$

where Z_A is the nuclear charge, and $\rho_A(\vec{r})$ is the spherically averaged atomic electron density centered on nucleus A. ρ_{pro} and ρ_{mol} are the summation 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 position.

All the present expressions are implemented in the standard computational chemistry package GAMESS [30]. Numerical calculations of the annihilation spectra are performed with a large but finite two-photon cut-off momentum: 10 au. This value is sufficient for the valence orbitals of the atoms and molecules studied. The core electron orbitals are characterized by large electron momenta, but in practice they contribute very little to be neglected in the annihilation spectra due to the repulsion from the nucleus. All the calculations have been proved to be accurate in our previous works [22–28]. However, in the present study, the calculations are based on the low-energy plane-wave positron approximation. Under this

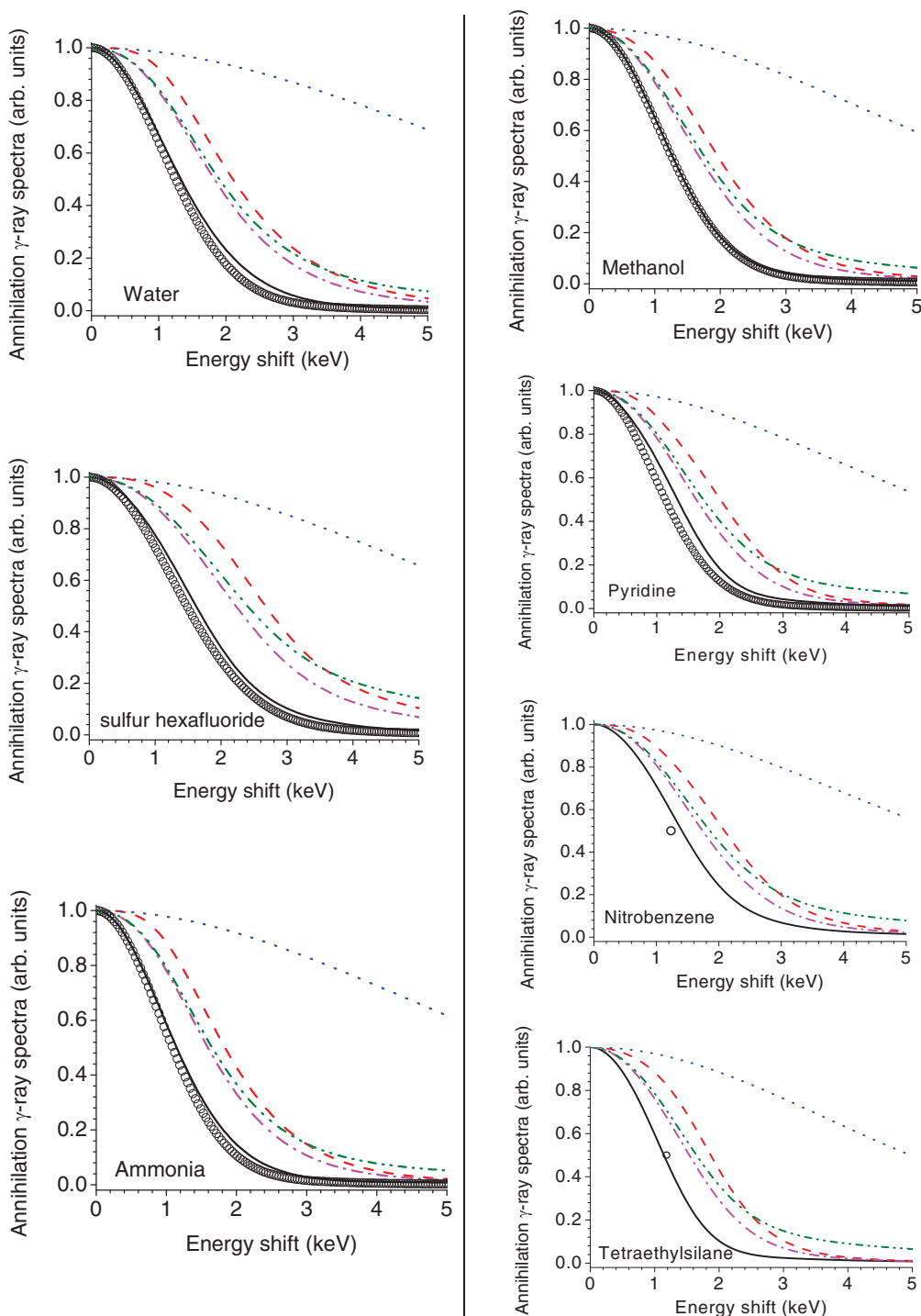


FIG. 4. Comparison of the theoretical γ -ray spectral profiles (lines) of small molecules H_2O , SF_6 , NH_3 , CH_3OH , $\text{Si}(\text{C}_2\text{H}_5)_4$, $\text{C}_5\text{H}_5\text{N}$, and $\text{C}_6\text{H}_5\text{NO}_2$ in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

approximation, the positron can be taken as a plane wave, and in the low positron momentum, the positron density could be unity everywhere.

III. RESULTS AND DISCUSSIONS

The γ -ray spectra profiles of 64 molecules have been theoretically studied in the present work including five molecules, which have no experimental measurements yet.

The remaining 59 molecules have accurate experimental γ -ray spectra measured in 1997 [12]. The contributions of each electron to γ -ray spectra in these molecules are not recognized and only the total spectra are given in their measurements [12]. It is difficult to analyze quantitatively the contribution of each electron from these total spectra in the positron-molecule annihilation process, although the valence electrons have more probability to annihilation with a positron than core electrons as known. However, the contributions of electrons

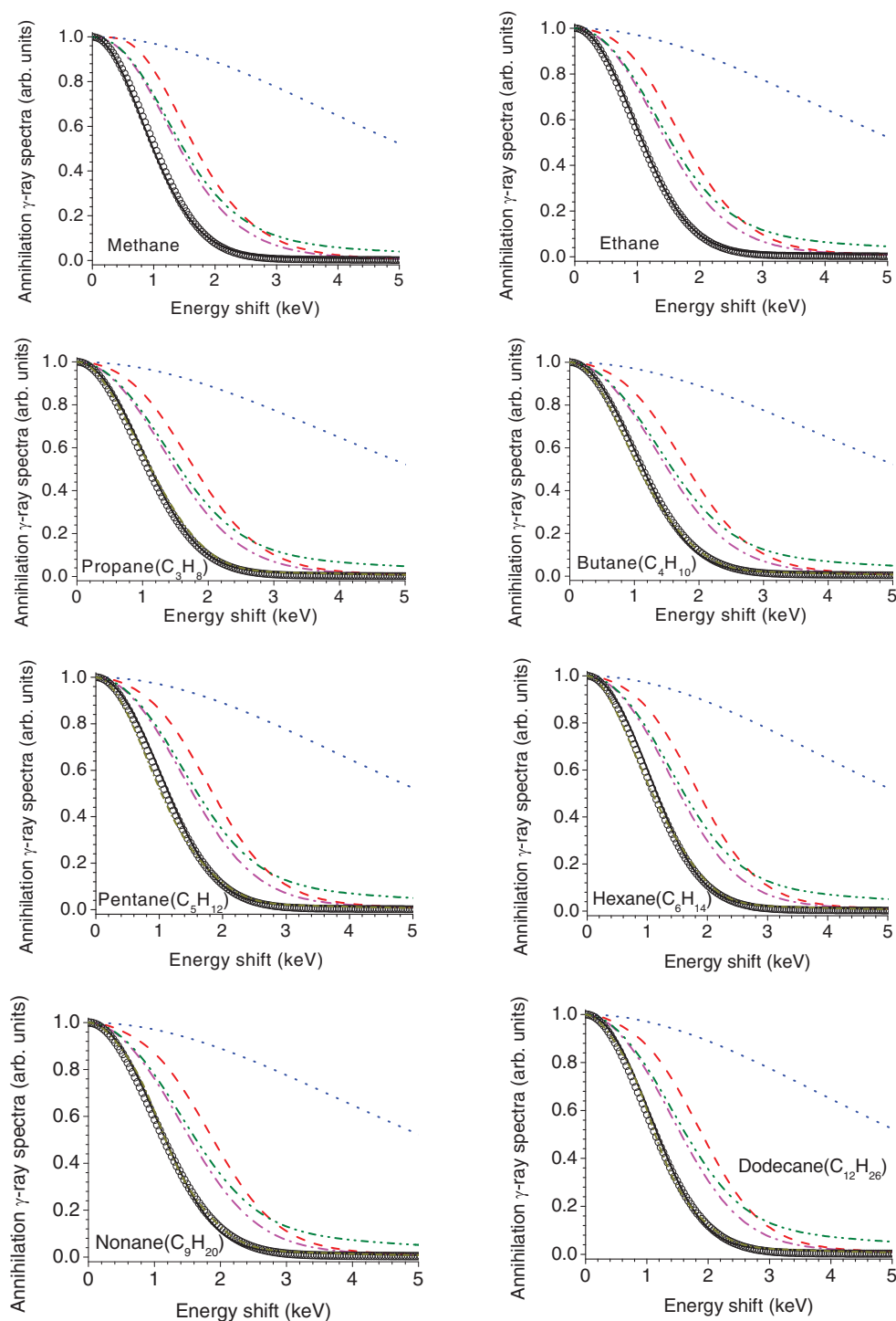


FIG. 5. Comparison of the theoretical γ -ray spectral profiles (lines) of linear alkane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

to annihilation process can be analyzed easily in theoretical study.

In the present study, five kinds of electrons in molecules, i.e., the outer valence electrons (red dashed lines) including the electrons in the highest occupied molecular orbital (HOMO), the inner valence electrons (black solid lines) including the electrons in the lowest occupied valence orbital (LOVO) [27], the total valence electrons (magenta dash-dotted lines), the

core electrons (blue dotted lines), and the total electrons (olive dash-dot-dot lines) are studied and compared with the corresponding experimental results (circles) [12] in order to get their contributions and correlations to the γ -ray spectra of molecules. The γ -ray line widths and the correlation coefficients of molecules are listed in Tables V and VI, respectively. The division of bound electrons is approximately due to the large energy gap between core, inner valence,

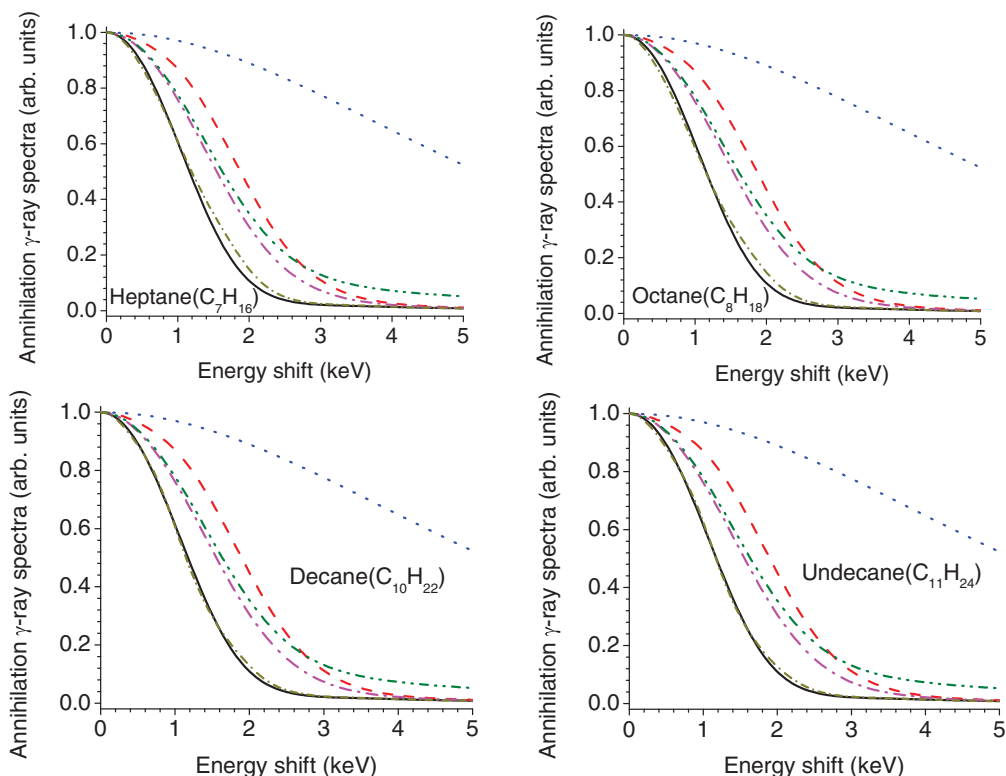


FIG. 6. The theoretical predictions of γ -ray spectral profiles of heptane, octane, decane, and undecane linear alkanes in positron-electron annihilation process.

and outer valence electrons and the composition of inner valence orbitals is usually dominated by the outermost s atomic orbitals. The electron configurations of all these electrons in all molecules are listed in Table VII.

A. Noble gases

For noble gas atoms, the inner valence electrons are also the electrons at LOVO while the outer valence electrons are only HOMO electrons as shown in Table VII. LOVO electrons are the special electrons [26] and constructed almost by the atomic outermost s electrons while HOMO electrons are constructed by the outermost p electrons under the linear combination of atomic orbital (LCAO) scheme. In the momentum representation, the outermost s -atomic electrons usually concentrate within the FWHM region while most of outer valence electrons distribute outside of the FWHM region. Figure 1 shows the theoretical γ -ray spectra of all the noble gas atoms compared with the two-Gaussian fitted experimental data [12]. There are no experimental data for the Rn atom, so only the theoretical predicted γ -ray spectra are given.

As shown in Fig. 2, the width of γ -ray spectra decreases slowly as the atomic number increases for noble gas atoms excluding neon. Under the low-energy positron plane-wave approximation, small width indicates that the low-momentum electrons have more probabilities to annihilate with positron. That is, for noble gas atoms, As the atomic number increases, the annihilating electrons are distributed more and more in the low-momentum region. Especially, the widths for inner valence electrons approach the experimental FWHM quickly

from Ne to Xe when the inner valence and outer valence electrons are different. According to the observations, the FWHM of Rn atom are predicted to be the inner valence electrons' width, i.e., 1.94 keV. This should be confirmed experimentally.

From helium to xenon, the profile correlation coefficient increases from 98.11 to 99.78. Helium has the worst profile quality among all the noble gas atoms compared with experiments. This might because there are only two bound electrons for helium, hence the electrons are pulled out easily off the atom by the incoming positron, which is less localized than the bound electrons. This effect will make the γ -ray spectra narrower [7]. Taking the positron attraction effect into account, the spectra will be suppressed. Hence, in the helium atom, the positron wave function and the interaction between helium and the positron must be considered in order to get an agreeable result. Recently, Dunlop *et al.* studied the first-order correlation corrections and got the agreeable prediction FWHM of 2.35 keV of the γ -ray spectra for helium [7].

Under the low-energy positron plane-wave approximation, this indicates that the positron has less and less effect on the bound electrons from helium to xenon. As the atomic number increases, the electrons feel stronger and stronger attractive force from the nucleus, the positron attraction even can be neglected. Hence, the plane-wave approximation is appropriate and more reasonable for these heavy atoms and the bound electrons will dominate the annihilation process rather than a positron. As shown in Fig. 2, the probability of the annihilating valence electrons distributing in the lower

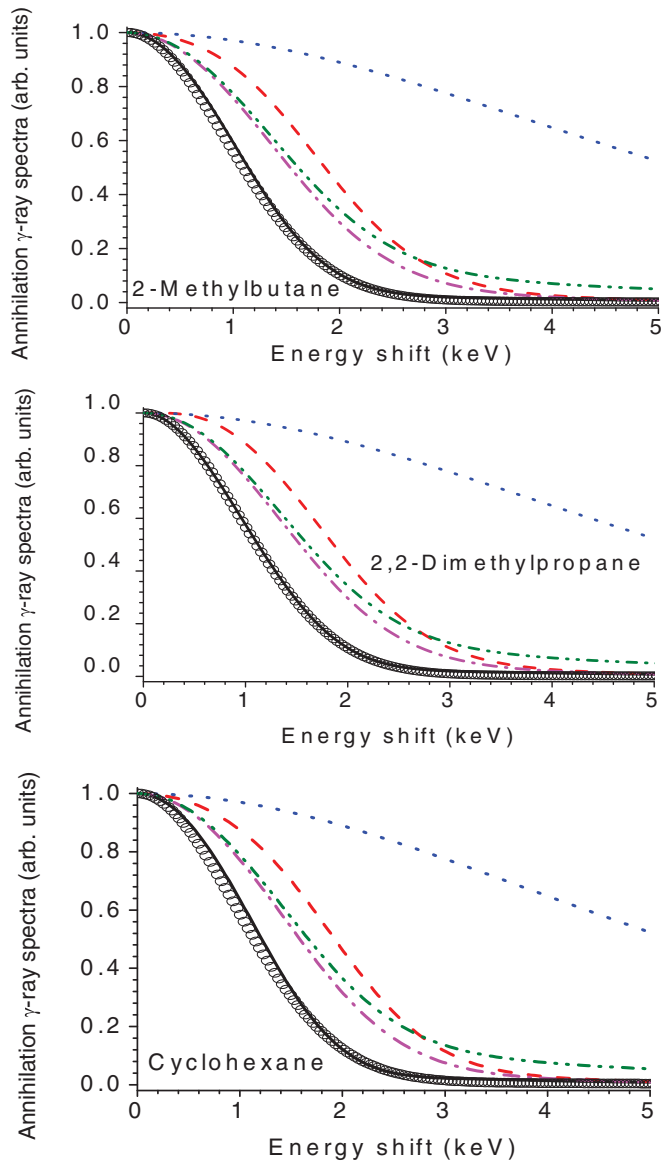


FIG. 7. Comparison of the theoretical γ -ray spectral profiles (lines) of 2-methylbutane, 2,2-dimethylpropane, and cyclohexane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

momentum region increases as atomic number increases for noble gas atoms Ne to Rn. Helium is a special one because its inner valence is the same as the outer valence. This indicates that the inner valence electrons distribute further from nuclear as the atomic number increases for noble gas atoms. Hence, the momentum of the annihilating bound electrons becomes smaller and smaller from Ne to Rn atoms. This makes neon have the widest width of γ -ray spectra among all noble gas atoms, which agrees well with the experimental results as shown in Fig. 2.

The predicted width of γ -ray spectra of helium is only 3.06 KeV, which is wider than the experimental one, i.e., 2.31 KeV. The about 30% of the relative difference could be from the neglecting of the positron wave function under the low-energy plane-wave approximation. The incoming positron

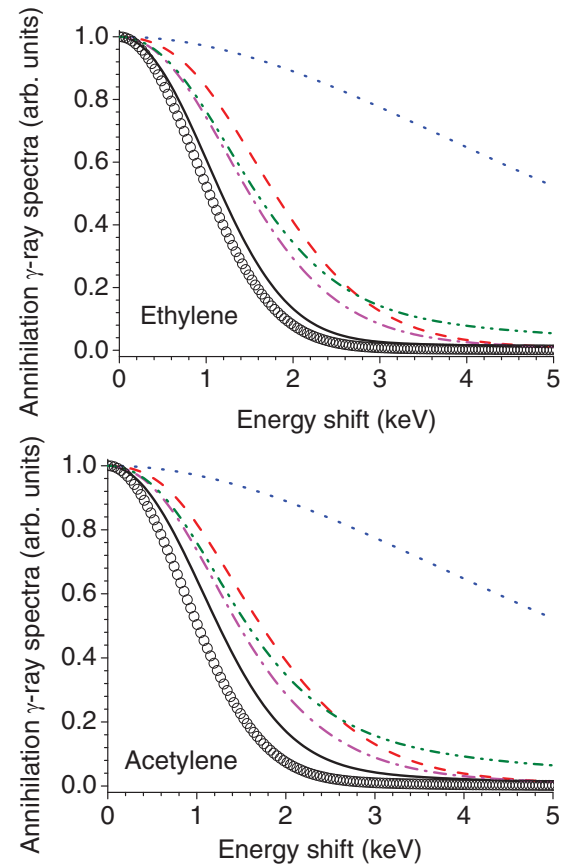


FIG. 8. Comparison of the theoretical γ -ray spectral profiles (lines) of ethylene and acetylene molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

will influence the bound electron more strongly in helium compared with other noble gas atoms. The wave function of bound electrons in helium will be distorted more due to the one-shell structure in helium. The positron wave function and the correlation effects between electrons and positron must be considered in helium. In the present work, the ratio of charge between one positron and all the positive charges are calculated. The ratio is $1/(2 + 1)$, about 33%; $1/(10 + 1)$, about 9%; $1/(18 + 1)$, about 5%; $1/(36 + 1)$, about 3%; $1/(54 + 1)$, about 2%; and $1/(86 + 1)$, about 1% from helium to radon respectively. This is to say that the interactions between a positron and electrons become less and less from 33% to 1% as the atomic number increases. Hence, the corrections of positron on the γ -ray spectra are about 33%, 9%, 5%, 3%, 2%, and 1% for He, Ne, Ar, Kr, Xe, and Rn, respectively. On the other hand, the relative differences of the width between experimental one and theoretical inner valence electrons are also calculated. They are $(3.06 - 2.31)/2.31$, about 33%; $(3.58 - 3.28)/3.28$, about 9%; $(2.46 - 2.31)/2.31$, about 6%; $(2.16 - 2.09)/2.09$, about 3%; and $(1.86 - 1.86)/1.86$, about 0% for He, Ne, Ar, Kr, Xe, and Rn, respectively. That is, the differences are 33%, 9%, 6%, 3%, and 0% for He, Ne, Ar, Kr, Xe, respectively, which almost agrees with the ratio of charge. This indicates that the inner valence electrons would dominate the annihilating process.

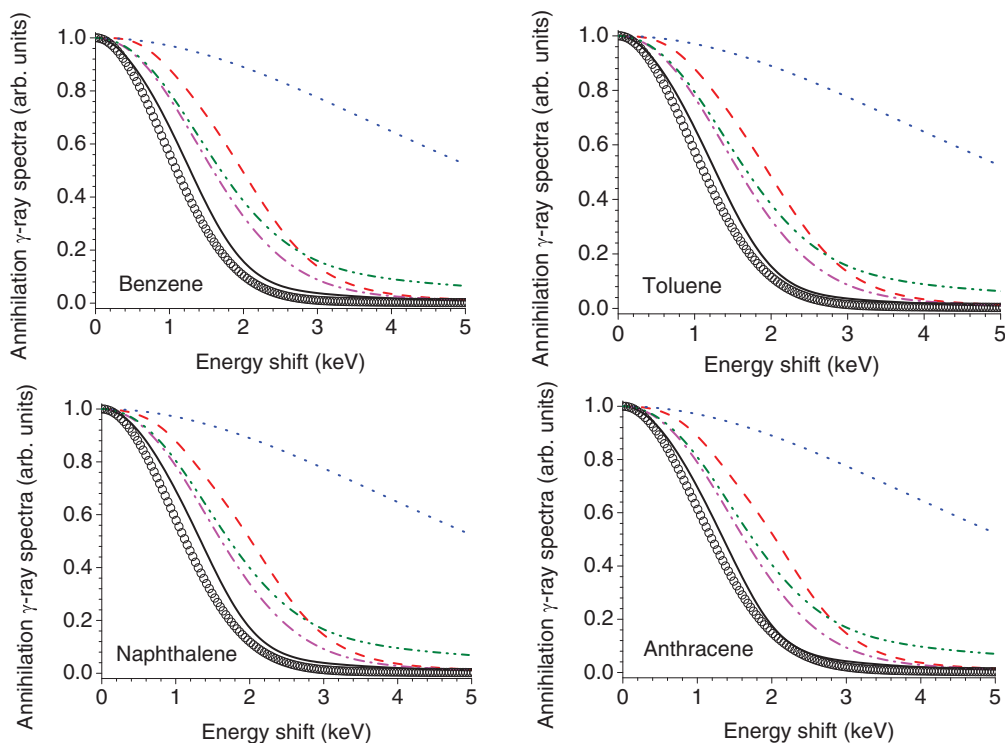


FIG. 9. Comparison of the theoretical γ -ray spectral profiles (lines) of naphthalene, benzene, anthracene, and toluene molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

Furthermore, the charge ratio decreases dramatically from He to Rn, which indicates that the correlation of positron with electrons becomes weaker and weaker as the atomic number increases. That is, neglecting the interaction between positron and electron is reasonable in large atomic number atoms. However, for light atoms, especially for He, the positron wave function should be considered in the positron-electron annihilation process. On the other hand, the difference between theoretical prediction and the experimental results is almost introduced by the neglecting of positron wave functions as shown in Table I.

Above 2 keV from Argon, there are another little peaks in the γ -ray spectra of inner valence electrons. In this high momentum region, only a little probability of the inner valence electrons is distributed. Hence, the inner valence electrons only play a little role in this high momentum region. However, most of the outer valence electrons are distributed here, the positron have more probabilities to annihilating with an outer valence electron rather than the inner valence electron. So in higher energy regions, the outer valence electrons will dominate the annihilating process. As shown in Fig. 1, when the total valence electrons are considered in the annihilating process, the theoretical γ -ray spectra of the total and outer valence electrons agrees better than the inner valence electrons with experiments. In noble gas atoms, the inner valence electrons are also the outermost s electrons while the outer valence electrons are the outermost p electrons. The outermost s electrons are almost distributed in lower momentum region while the outermost p electrons are almost distributed in higher momentum region. Because most of the inner valence are distributed within the FWHM region, the inner valence electrons will dominate the width of γ -ray as shown in Table I. In the higher region, the

outer valence electrons should be considered to improve the agreement with the experimental measurements.

B. Some small molecules

The electron density distributions of noble gas atoms are in spherical symmetry whether in coordinate space or momentum space. However, for multicentered systems, the electron density is multicentered while the momentum distribution of electrons is still one-centered. The outermost s and p electrons of atoms in molecules could be hybridized. Hence, the inner valence and outer valence electrons are more complex than in the noble gas atoms. Does these two kind of electrons play the similar roles in the γ -ray spectrum of multicentered systems?

First, we studied the positron-electron annihilating process in 12 small molecules including H_2 , N_2 , O_2 , CO , CO_2 , H_2O , SF_6 , NH_3 , CH_3OH , $Si(C_2H_5)_4$, $C_6H_5NO_2$, and C_5H_5N as shown in Figs. 3 and 4. One can see that the inner valence electrons in these molecules are still the most agreeable with experiments among all electrons, especially for H_2O , SF_6 , NH_3 , and CH_3OH [23] molecules. This is probably due to the spherical symmetry of the momentum distribution as shown in Fig. 5. However, there are still larger difference between the experimental results and the γ -ray spectra of the inner valence electrons, especially in H_2 , N_2 , O_2 , CO , CO_2 molecules. It is interesting that, just like the noble gas atoms, in all these molecules, the widths of the γ -ray spectra for all kinds of electrons are larger than the corresponding experiments.

The hydrogen molecule has two electrons distributed around two centers. Although helium has two electrons too, which are distributed only around one centers. These two electrons of both molecules are made of $1s$ electrons of atoms.

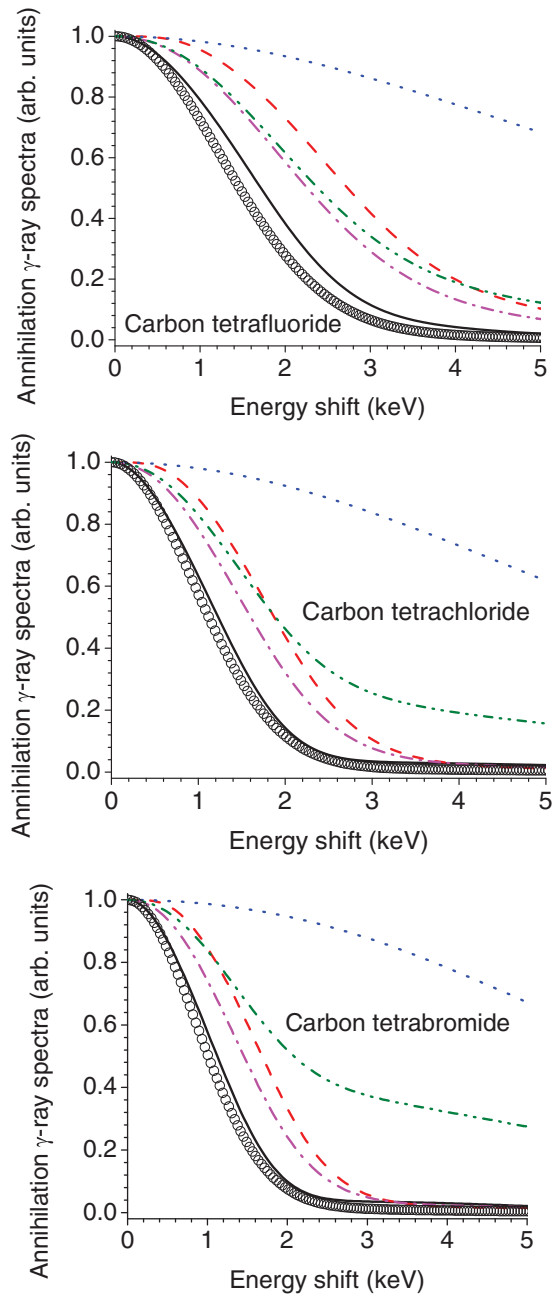


FIG. 10. Comparison of the theoretical γ -ray spectral profiles (lines) of CF_4 , CCl_4 , and CBr_4 molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

The positron has the same charges as the hydrogen molecule, hence the positron would perturb the electrons as strong as the nuclear. In these two light molecules, helium or hydrogen atoms, the correlation effects between positron and electrons must be considered. This can explain why the theoretical γ -ray spectra agree not well with the experiments without the consideration of the correlation of the positron.

The molecular orbitals of nitrogen, oxygen, carbon monoxide, and carbon dioxide are hybridized by the outermost s and p electrons of the corresponding atoms. The outermost s or p electrons are not the proper terms anymore. In the present study, the inner valence and the outer valence are

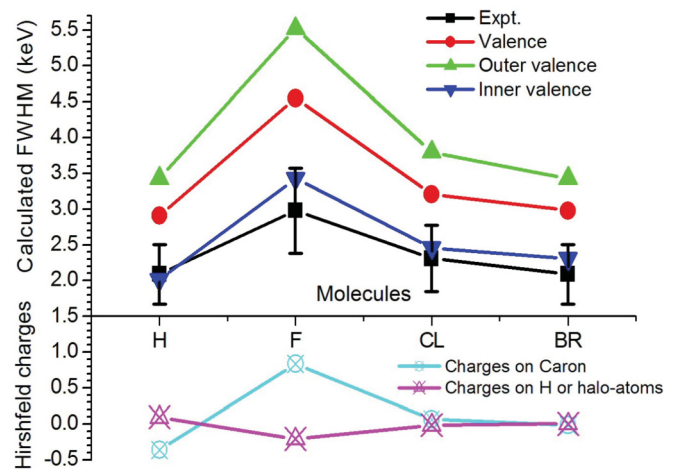


FIG. 11. Comparison of the theoretical and experimental FWHM of γ -ray spectra of methane and its halocarbons. The error bars show that the calculated values of the inner valence electrons are about 20% agreement with the experiments [12]. The Hirshfeld charges are also plotted to show the relationship between the annihilation site and the spectra.

used instead of the outermost s and p electrons because the most composition of the inner valence electrons and the outer valence electrons are outermost s and p electrons, respectively. In these molecules, the inner valence electrons have the most agreeable γ -ray spectra in all electrons, although not good enough compared with noble gas atoms. In noble gas atoms, the inner valence electrons are pure outermost s electrons while the inner valence electrons are hybridized for these molecules. The sp hybrid in the inner valence orbitals makes the γ -ray spectra wider than the experiments. In these molecules, the positron wave functions must be considered and supposed to influence the p electrons much stronger.

The γ -ray spectra of some small inorganic and organic molecules are also studied as shown in Fig. 4. The inner valence electrons of these molecules agree well with the corresponding experiments (there are only one-Gaussian fit experimental data for nitrobenzene [12]). The correlation coefficients are all almost 99.9% for these inner valence electrons. According to the orbital structures, the most parts of the inner valence electrons are the outermost s electrons for all these molecules. The same as the above atoms and molecules, the outermost s electrons are mainly distributed in the low momentum region. These inner valence electrons have the most probabilities to annihilate a positron under the plane-wave approximation and give the most agreeable prediction of γ -ray spectra among all electrons. The γ -ray spectra for each kind of electrons almost have the same behavior for these molecules. In these molecules, whatever for F, S, N, O, the outermost s electrons are the $2s$ electrons. These outermost $2s$ electrons might play important role in the positron-electrons annihilation process in these molecules. Even for all the following molecules, the width of γ -ray spectra of the inner valence electrons have almost the equivalent width of the experiments. Another interesting phenomenon is that almost all the γ -ray spectra of the inner valence electrons are wider than the corresponding experiments. That means

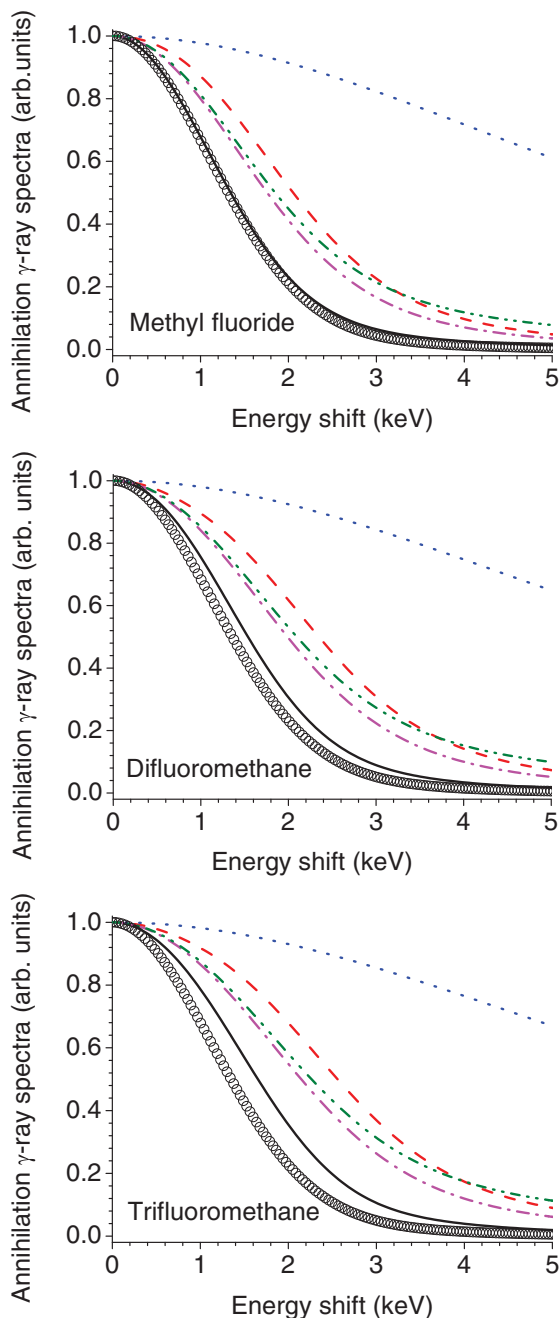


FIG. 12. Comparison of the theoretical γ -ray spectral profiles (lines) of methyl fluoride, difluoromethane, and trifluoromethane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

that the positron will turn p electrons into s electrons if the positron-electron interactions are considered in order to get agreeable results. Hence, under the low-energy plane-wave approximation, the theoretical γ -ray spectra will be wider than the experiments.

C. Linear alkanes

In order to confirm the importance of the inner valence electrons in positron-electrons annihilation process in molecules, the γ -ray spectra of series of linear alkanes,

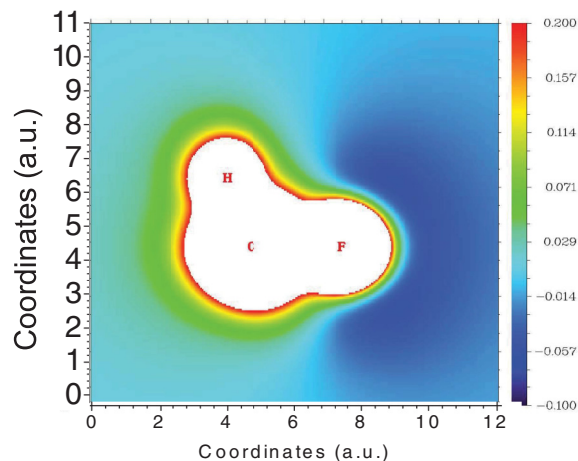


FIG. 13. The contour color-filled map of the electrostatic potential (ESP), i.e., the negative local molecular attraction potential (LMAP) on F-C-H plane of methyl fluoride.

C_nH_{2n+2} ($n = 1-12$) are studied [22,24,25]. Methane (CH_4) is the smallest alkane that possesses only the C-H bonds. It has been the prototype molecule in the history of chemical research. Such structural characteristics of linear alkanes enable us to study the C-H bonds and the C-C bonds in positron-electron annihilation process. As shown in Fig. 5, accurate γ -ray experimental measurements are available for methane to hexane ($n = 1-6$), nonane ($n = 9$), and dodecane ($n = 12$). In Fig. 5, the calculated spectra of inner valence electrons of these eight alkanes are in excellent agreement with available experimental measurements whether the chain is long or short. The agreement is as good as methane. The experimental widths of γ -ray spectra for C_3H_8 , C_5H_{12} , and C_6H_{14} [24] are the same, i.e., 2.24 keV. Furthermore, for C_2H_6 , C_4H_{10} , C_9H_{12} , and $C_{12}H_{26}$, the experimental widths are also almost the same, about 2.31 keV. For all these linear alkanes molecules, the width of the core electrons are all 10.44 keV. This might indicate that the composition of these core electrons for all these molecules are almost the same.

In methane, the dominant contribution on positron-electron annihilation process is from the $2s$ electrons of carbon atoms [22]. In these linear alkanes, indeed, the inner valence electrons are made of $2s$ electrons of carbon atoms. The length of carbon chains of these molecules has only little effect on the positron-electron annihilation process. The experimental measurements agree well with the corresponding inner valence electrons of these linear alkanes. The inner valence electrons might play more important role in the positron-electron annihilation process under the low-energy positron plane-wave approximation. Hence, it is reasonable to predict the widths with the inner valence electrons, whereas the alkanes with $n = 7, 8, 10$, and 11 , that is, heptane (C_7H_{16}), octane (C_8H_{18}), nonane (C_9H_{20}), and undecane ($C_{11}H_{24}$) as shown in Fig. 6, do not have such the measurements. Following these roles, the predicted width is about 2.39 keV for these four linear alkanes.

D. Isomers and structure effects

The inner valence electrons are found to be well agreeable with the experimental measurements in γ -ray spectra [22-26].

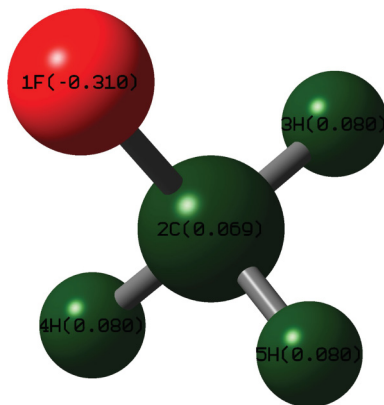


FIG. 14. Hirshfeld charges (a.u.) and the molecular structure of methyl fluoride.

These inner valence electrons of linear alkanes are almost made of the $2s$ electrons of carbon atoms. The effects of the length of carbon chain are almost zero on γ -ray spectra. That is, the structures of molecules and the electron distributions in coordinate space are not the important factor in the positron-electron annihilation process. As shown in above expressions,

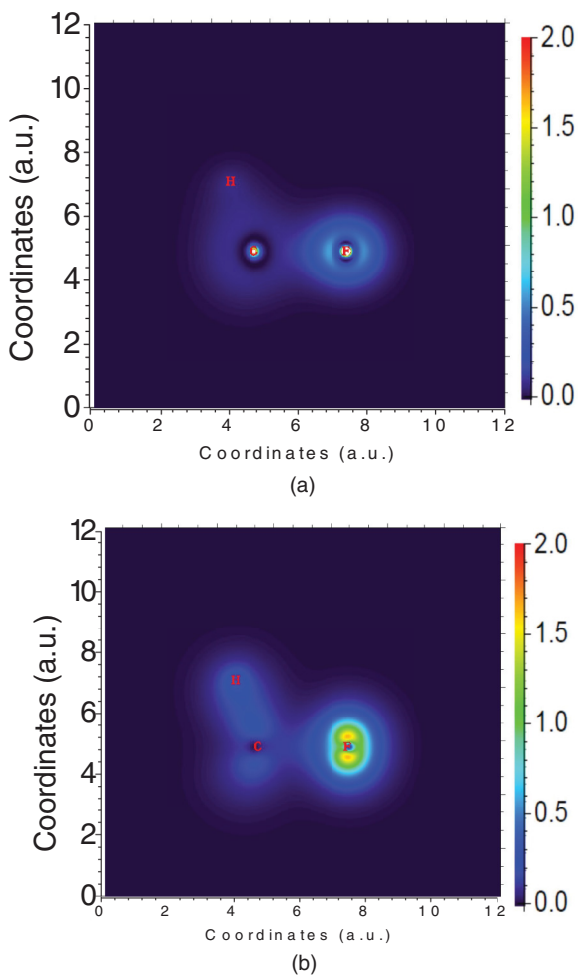


FIG. 15. The electron density distributions on F-C-H plane of (a) outer valence and (b) inner valence electrons.

the γ -ray spectra are directly related with the momentum distribution of bound electrons under the low-energy positron plane-wave approximation. The momentum distribution is a single-center physical property, and the coordinate space will have almost no effects in the momentum distribution. Hence, the character of the momentum distribution will determine the γ -ray spectra neither the molecular and electronic structures.

The composition of inner valence electrons and the variation of γ -ray spectra are also represented for more hydrocarbon molecules as shown in Figs. 7–9. The three five-carbon alkane isomers [8] have the same γ -ray spectra whether for the core or the inner valence and outer valence electrons while their molecular and electronic structures are dramatically different from our previous studies. For all these five-carbon alkane isomers, the core electrons are almost made of the carbon $1s$ atomic orbitals, and the inner valence electrons are almost dominated by the valence $2s$ electrons of carbon atoms while the outer valence electrons are dominated by the outermost $2p$ electrons. This is one of the reasons why the isomers with different molecular structures have almost the same γ -ray spectra. The other reason is that in momentum space, i.e., the one-center momentum space, all the electron densities around each center are summed or integrated into the same center, the molecular structures and symmetries become more difficult to be recognized in the γ -ray spectra. Moreover, in order to obtain the γ -ray spectra from the momentum distribution, a double integration and spherically averaged operations are performed because the experiments are performed. The difference of the momentum distributions of three isomers has been shrunk in the γ -ray spectra, which make the γ -ray spectra become almost the same. In the experimental results, these three isomers also have the same γ -ray spectra. The inner valence electrons dominate the γ -ray spectra has already been proven in our previous works.

Even the widths of the γ -ray spectra of C_6H_{12} , $C_6H_5CH_3$, C_7H_8 , and $C_{10}H_8$ have the same experimental value, about 2.31 keV as the linear alkanes C_4H_{10} , C_9H_{12} , and $C_{12}H_{26}$. Hence, the γ -ray spectra show only some effects of the structures of molecules. These spectra show the dominance of the $2s$ electrons of carbon atoms in these hydrocarbon molecules. That is supposing that the positron can penetrate deeper inside the atom and the annihilation rate can be enhanced strongly when the correlation effects are considered.

E. Halogenated carbons

In order to clarify the contribution of hydrogen atom on the γ -ray spectra in the positron-electron annihilation

TABLE II. Composition (%) of valence orbitals of CH_3F .

Basis sets	$3a'$	$4a'$	$1a''$	$5a'$	$6a'$	$2a''$	$7a'$
F1_2S	90.6	4.3	—	—	1.9	—	—
F1_2P	—	13.6	63.6	63.6	60.9	34.3	34.3
C1_2S	9.4	53.2	—	—	2.3	—	—
C1_2P	—	—	23.7	23.7	24.1	29.3	29.3
H1_1S	—	9.5	—	8.4	3.7	—	24.1
H2_1S	—	9.5	6.3	2.1	3.7	18.1	6.1
H3_1S	—	9.5	6.3	2.1	3.7	18.1	6.1

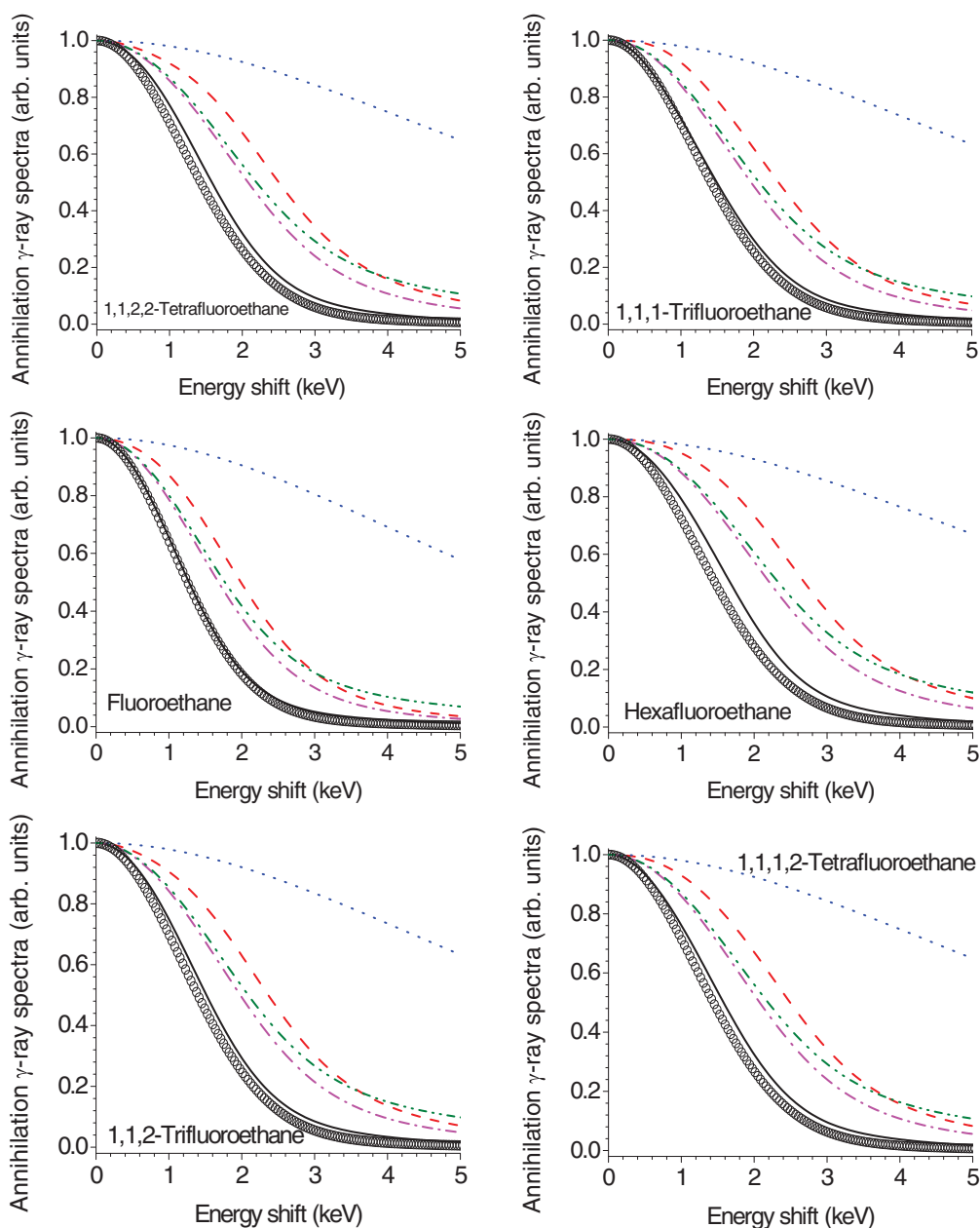


FIG. 16. Comparison of the theoretical γ -ray spectral profiles (lines) of fluoroethane, 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,2,2-tetrafluoroethane, and hexafluoroethane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

process, the theoretical γ -ray spectra of 25 halocarbons are also studied in the present work, as shown in Figs. 10–23. The fully substituted halocarbons of methane, CF_4 [27], CCl_4 , and CBr_4 are shown in Fig. 10 [29]. Compared with methane, the γ -ray spectra have some different behavior. The positrophilic site has been changed from carbon atoms to halo-atoms as shown in Fig. 11 [29]. This is because halo-sites have more negative charge than the carbon atoms. However, the outermost s electrons in carbon or halogen atoms still dominate the γ -ray spectra. For CCl_4 and CBr_4 , there are many core electrons, which make the total γ -ray spectra converge slowly in large momentum region. That makes the small difference of the total γ -ray spectra between CCl_4 and CBr_4 and CF_4 .

F. Partially fluorinated methanes

As is well known, methane does not have permanent dipole, positrons have been confirmed to annihilate with the inner valence electrons $2a_1$ [22]. However, methyl fluoride has permanent dipole and atom fluorine is negatively charged. Would atom fluorine or carbon has the same behavior within methane? Which electrons will dominate the annihilation process?

Taking fluorine as an example as shown in Fig. 12, the experimental results agree well with the inner valence electrons when only one hydrogen atom is substituted by fluorine atom. However, as two or more fluorinate atoms are substituted into hydrocarbons, the agreement becomes worse and worse. This

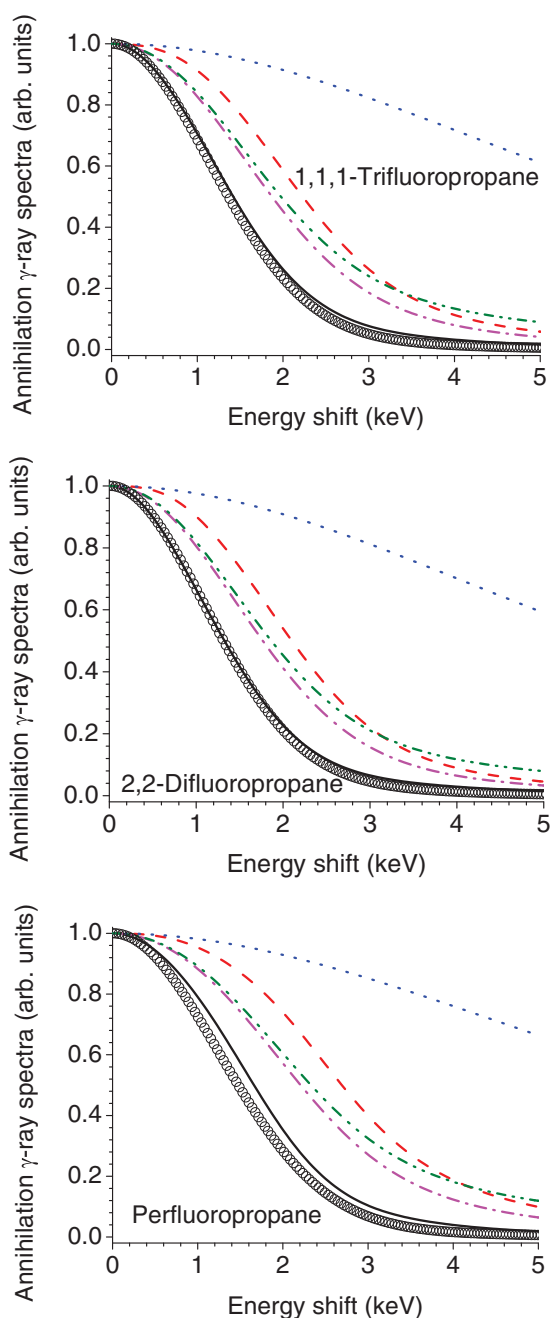


FIG. 17. Comparison of the theoretical γ -ray spectral profiles (lines) of 1,1,1-trifluoropropane, 2,2-difluoropropane, and perfluoropropane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

can be explained that the outermost s electrons in fluorine and carbon atoms might not be influenced strongly when only one or two fluorines substitute into hydrocarbons. This is because that the outer valence p electrons can be influenced more strongly than the inner valence electrons. The experimental γ -ray spectra agree well with the inner valence electrons. However, when the substituted fluorine are more than two, the $2s$ electrons of carbon atom will be hybrid with $2p$ electrons of fluorine. The momentum distributions of the inner valence electrons will have more p momentum characters. Hence, the

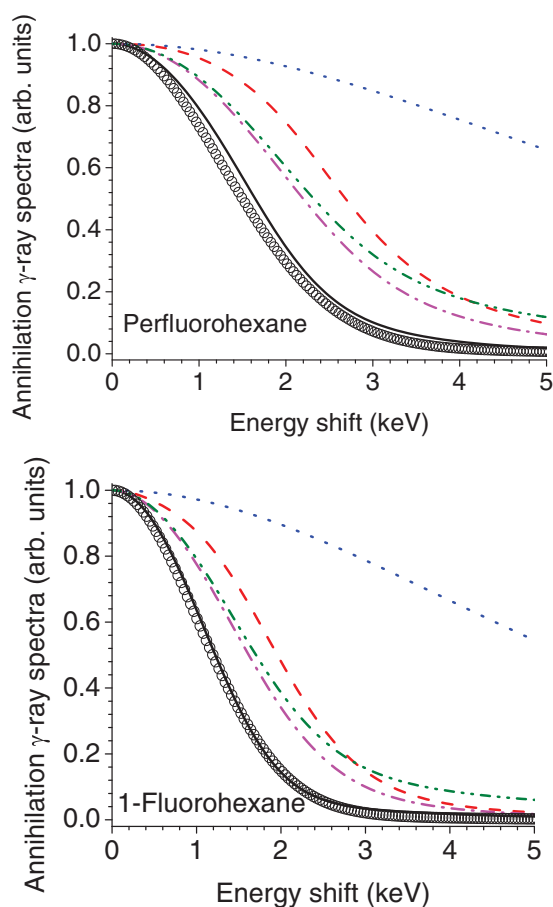


FIG. 18. Comparison of the theoretical γ -ray spectral profiles (lines) of 1-fluorohexane and perfluorohexane molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

theoretical γ -ray spectra of inner valence will be wider than the experimental results.

As shown in Fig. 13, the electrostatic potential in methyl fluoride has been calculated. The negative ESP potential is dominantly distributed around the outside of the fluorine atom for a long range. In this region, the LMAP is positive, which means this area is the positrophilic site of this molecule. The positron will be attracted into this site to annihilate electrons. However, are there enough electrons, especially the weakly bound electrons, in this positrophilic site?

As shown in Fig. 14, the Hirshfeld charges of methyl fluoride have been labeled on each atom. Compared with the methane molecule, as one can see, the C-H bond is a polar bond with a partial negative charge -0.363 a.u. on the central carbon. In methyl fluoride, however, the C-H bonds are not polar bonds anymore. The carbon atom and hydrogen atoms are all positively charged and part of the electrons on these atoms have been attracted onto the fluorine atom. About -0.310 a.u. negative charge is on the fluorine atom, because the fluorine atom of methyl fluoride is a positrophilic site as shown by LMAP, and there are also extra electrons in this area. Hence, the combination of LMAP and Hirshfeld charge shows that electrons on the fluorine atom will dominate the annihilation process.

TABLE III. Composition (%) of inner valence orbitals of 1-fluorohexane.

Basis sets	8a'	9a'	10a'	11a'	12a'	13a'	14a'
F1_2S	90.4	–	2.5	1.6	1.3	–	–
C2_2S	–	22.8	4.3	12.7	7.7	9.4	6.6
C3_2S	–	21.1	6.9	11.3	8.7	–	14.1
C4_2S	–	17.1	18.5	2.0	7.1	14.6	–
C5_2S	–	12.1	20.5	2.2	5.2	8.7	13.0
C6_2S	5.5	5.5	12.6	17.3	15.9	2.9	–
C7_2S	–	4.5	16.7	19.6	14.9	5.7	3.0
H8_1S	–	2.4	–	1.5	1.1	3.3	3.8
H9_1S	–	2.4	–	1.5	1.1	3.3	3.8
H10_1S	–	2.0	–	1.5	1.1	–	6.9
H11_1S	–	2.0	–	1.5	1.1	–	6.9
H12_1S	–	1.5	1.9	–	1.1	5.5	1.0
H13_1S	–	1.5	1.9	–	1.1	5.5	1.0
H14_1S	–	1.2	2.3	–	–	2.4	5.8
H15_1S	–	1.2	2.3	–	–	2.4	5.8
H16_1S	–	–	1.4	2.6	3.7	2.4	–
H17_1S	–	–	1.4	2.6	3.7	2.4	–
H18_1S	–	–	1.5	2.9	3.7	1.7	–
H19_1S	–	–	1.6	2.6	2.6	1.9	6.1
H20_1S	–	–	1.6	2.6	2.6	1.9	6.1
F1_2P	–	–	–	4.1	8.9	6.3	–
C2_2P	–	–	–	–	3.1	3.3	4.9
C3_2P	–	–	–	1.6	1.5	2.3	6.5
C4_2P	–	–	–	3.6	1.3	3.6	1.8
C5_2P	–	–	–	3.4	1.2	–	5.3
C6_2P	4.1	–	–	–	–	5.8	–
C7_2P	–	–	–	–	–	2.0	2.5

The inner valence and outer valence electrons have different behavior, especially in the momentum space. The electron density distributions on the F-C-H plane for inner valence and outer valence electrons are shown in Fig. 15. Most of electrons are distributed around fluorine atom in the coordinate space whatever for inner valence and outer valence. As shown in Fig. 12, the fluorine atom is the positrophilic site for the annihilation process. Hence, the inner valence electrons and the outer valence electrons distributed around the fluorine atom have the same probability to annihilate with the positron. However, as shown in Fig. 13, the γ -ray spectra of the inner valence electrons agree 99.94% with the experiments while the valence electrons only have 95.67% agreement with the same experimental measurement.

The γ -ray spectra are usually determined by the momentum distribution of the low-energy region. According to the momentum distribution characteristics, the atomic s electrons have a maximum distribution at the zero point in the momentum space, then the momentum distributions decrease rapidly. So most of the momentum distribution of s electrons are distributed in the low-energy region. However, the atomic p electrons have a minimum distribution at the zero point, which makes the momentum distribution only have a little contribution to the γ -ray.

As shown in Table II, because the fluorine atom is the positrophilic site, we only focus on the fluorine atom; the composition of valence electrons is given. For the inner valence electrons, 3a' is made of 90.6% $2s$ electrons of the fluorine atom and 9.4% $2s$ electrons of atomic carbon. Hence, the

$2s$ electrons of the fluorine atom dominate the annihilation process. Because the carbon atom is not the positrophilic site, although 4a' is also the inner valence electron with 53.2% $2s$ electrons of the carbon atom, only 13.6% $2p$ electrons of the fluorine atom contribute to annihilation. While for the outer valence electrons, as shown in Table II, the positrophilic site is made of $2p$ of carbon and fluorine atoms, and $2p$ electrons contribute a little in the low-energy region. This is the reason why the outer valence electron disagrees with the experiments.

Although the valence electrons of methyl fluoride take part in the annihilation process, the $2s$ electrons of fluoride atom have most of the contribution to the γ -ray spectra. For methyl fluoride, the inner valence electrons are almost dominated by the valence $2s$ electrons while the outer valence electrons are dominated by the outermost $2p$ electrons. This is one of the reasons why the inner valence electron agrees well with experiments while the outer valence electrons do not.

G. Fluorinated ethanes

Figure 16 shows the γ -ray spectra of some fluoroethanes. As the number of substituted fluorine atoms increases from 1, 3, 4, to 6, the experimental widths of the γ -ray spectra increase from 2.54 keV, 2.83 keV, 2.91 keV, to 2.98 keV [12]. The present theoretical widths of the inner valence electrons also show the same increasing variation from 2.61 keV, 3.06 keV, 3.21 keV, and 3.36 keV. As one can see, the width of the γ -ray spectra is not sensitive to the position of the substituted fluorine atoms. 1,1,1-trifluoroethane and 1,1,2-trifluoroethane

TABLE IV. Composition (%) of outer valence orbitals of 1-fluorohexane

Basis sets	1a''	15a'	16a'	2a''	3a''	17a'	18a'	4a''	19a'	5a''	20a'	6a''	7a''	21a'	22a'
F1_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C2_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C3_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C4_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C5_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C6_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C7_2S	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H8_1S	-	-	-	4.9	3.4	1.0	-	1.3	2.1	3.9	1.8	4.3	5.7	-	-
H9_1S	-	-	-	4.9	3.4	1.0	-	1.3	2.1	3.9	1.8	4.3	5.7	-	-
H10_1S	-	-	-	6.0	-	-	2.9	4.8	-	2.5	-	-	10.2	5.6	-
H11_1S	-	-	-	6.0	-	-	2.9	4.8	-	2.5	-	-	10.2	5.6	-
H12_1S	2.1	-	-	1.1	4.4	-	2.2	3.2	-	-	4.4	10.3	1.6	1.7	-
H13_1S	2.1	-	-	1.1	4.4	-	2.2	3.2	-	-	4.4	10.3	1.6	1.7	-
H14_1S	-	-	-	4.4	4.6	1.7	-	-	-	1.9	2.7	3.8	8.8	4.3	-
H15_1S	-	-	-	4.4	4.6	1.7	-	-	-	1.9	2.7	3.8	8.8	4.3	-
H16_1S	6.2	4.2	-	-	-	-	-	3.4	2.2	8.3	1.9	6.6	-	-	-
H17_1S	6.2	4.2	-	-	-	-	-	3.4	2.2	8.3	1.9	6.6	-	-	-
H18_1S	-	-	-	-	-	17.8	-	-	9.8	-	-	-	-	1.0	5.6
H19_1S	-	-	-	1.6	4.9	2.4	2.2	6.2	1.7	5.6	2.7	2.8	2.8	1.7	-
H20_1S	-	-	-	1.6	4.9	2.4	2.2	6.2	1.7	5.6	2.7	2.8	2.8	1.7	-
F1_2P	48.0	62.3	59.9	7.7	11.9	4.7	2.1	14.5	13.7	11.3	3.2	3.9	-	-	4.9
C2_2P	2.5	2.6	2.4	13.6	8.6	7.6	17.4	4.2	15.0	9.1	9.0	6.2	7.8	13.7	15.8
C3_2P	-	-	1.2	19.2	-	11.5	19.6	11.6	6.7	5.7	-	-	14.9	20.6	20.1
C4_2P	5.2	2.0	12.2	4.7	15.9	-	13.8	10.6	14.5	-	20.2	15.1	2.1	5.8	13.7
C5_2P	-	-	1.2	13.5	14.3	14.4	16.1	-	1.6	3.9	15.6	6.7	13.1	16.2	16.6
C6_2P	25.9	22.0	15.9	-	-	1.3	-	5.3	11.0	12.3	8.5	7.7	-	1.1	9.5
C7_2P	-	-	-	4.8	13.1	30.2	14.4	14.9	13.9	10.9	15.7	4.5	3.7	6.0	11.7

have the same width of the γ -ray spectra showing both in the experiments and the predicted results, although the positrons of fluorine atoms are dramatically different. The same phenomenon is also observed in 1,1,1,2-tetrafluoroethane and 1,1,2,2-tetrafluoroethane. There are strong correlations between the inner valence electrons and the positron-electron annihilation.

H. Partially fluorinated propanes

In Fig. 17, the γ -ray spectra of partially substituted propane molecules with two or three fluorine atoms, and fully substituted propane have been compared with the recent experimental measurements [12]. The γ -ray spectra of 2,2-difluoropropane have been already compared with propane and experimental results in our previous study [28]. The fluorine atoms of these three molecules are the positrophilic sites where the positron prefers to approach and annihilate in these region. For fully substituted propane, i.e., perfluoropropane, part of $2p$ electrons of carbon atoms will hybrid with the $2s$ electrons of fluorine atoms. The inner valence electrons have more p -orbital composition, which makes the momentum distribution wider to the high-energy region.

I. Fluorinated hexanes

The 1-fluorohexane molecule has more than one negatively charged ends of C-H bonds or C-F bond. For such large molecules, is it still true that positron annihilates in these

areas? Because the bound electrons are distributed all over of the molecule, is it still true that the outermost s electrons of this molecule dominate the annihilation process? Our aim is to reveal the mechanism of the annihilation process in this molecule and confirm the observation in the experimental measurements [12]. In Fig. 18, the γ -ray spectra of 1-fluorohexane in the positron-electron annihilation process for core, inner valence, and outer valence electrons are compared with the experimental measurements [12]. The experimental FWHM 2.46 keV, is exactly the same with the prediction of the inner valence electrons. The whole profile of γ -ray spectra of inner valence electrons agrees well with experiment as 99.97%. The outer valence electrons agree only 95.00%

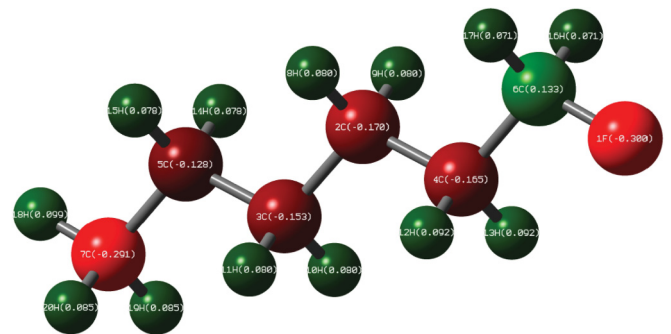


FIG. 19. Hirshfeld charges (a.u.) and the molecular structure of 1-fluorohexane.

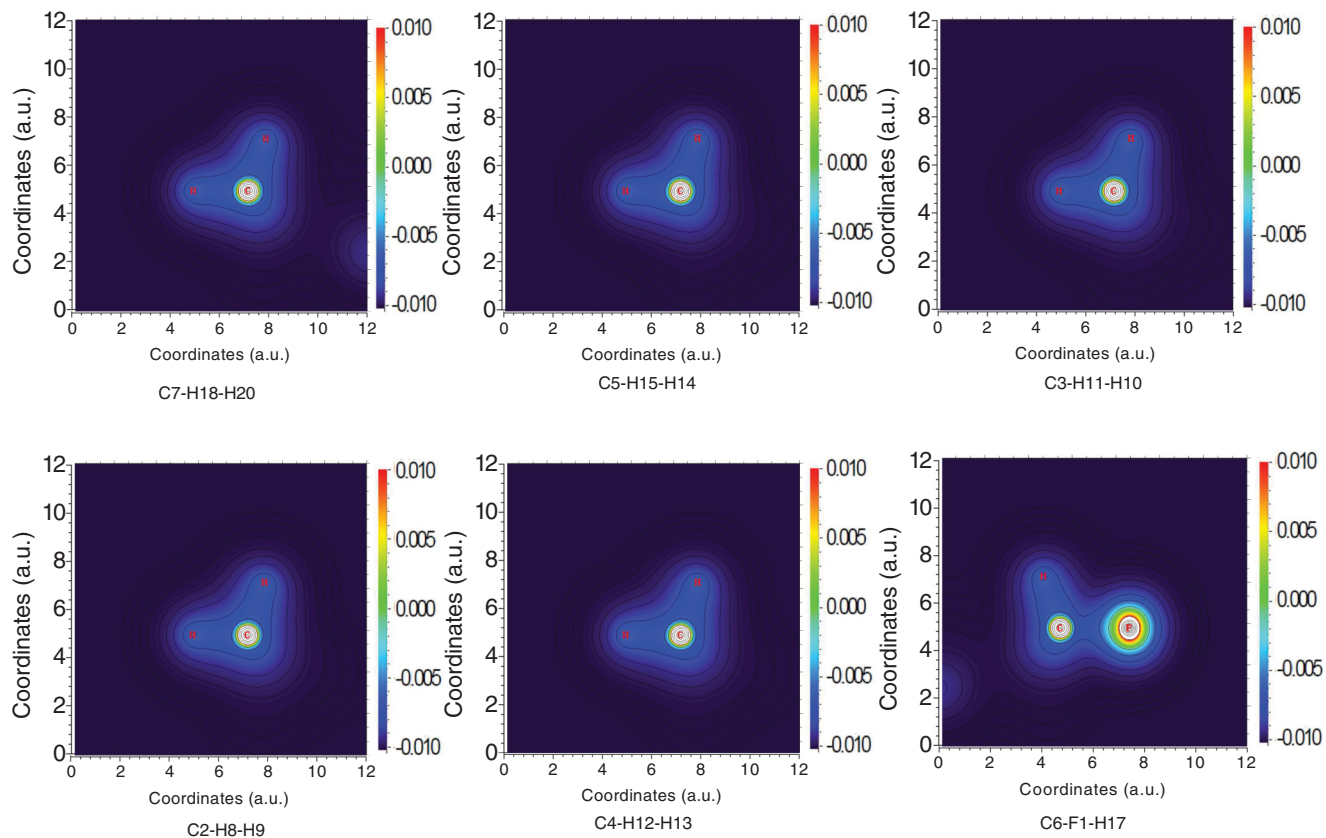


FIG. 20. The electron density distribution on different planes of 1-fluorohexane.

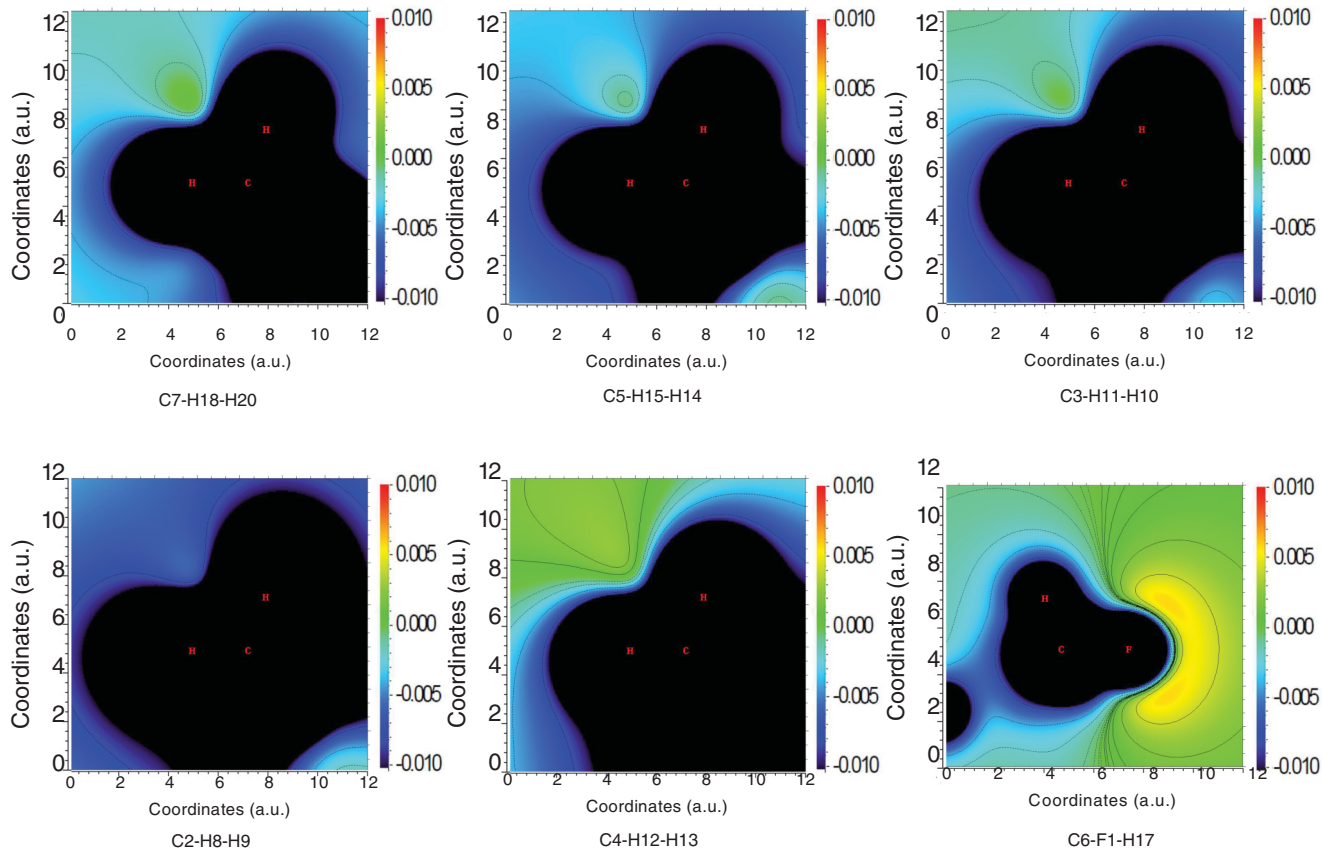


FIG. 21. The local molecular attraction potential (LMAP) on different planes of 1-fluorohexane.

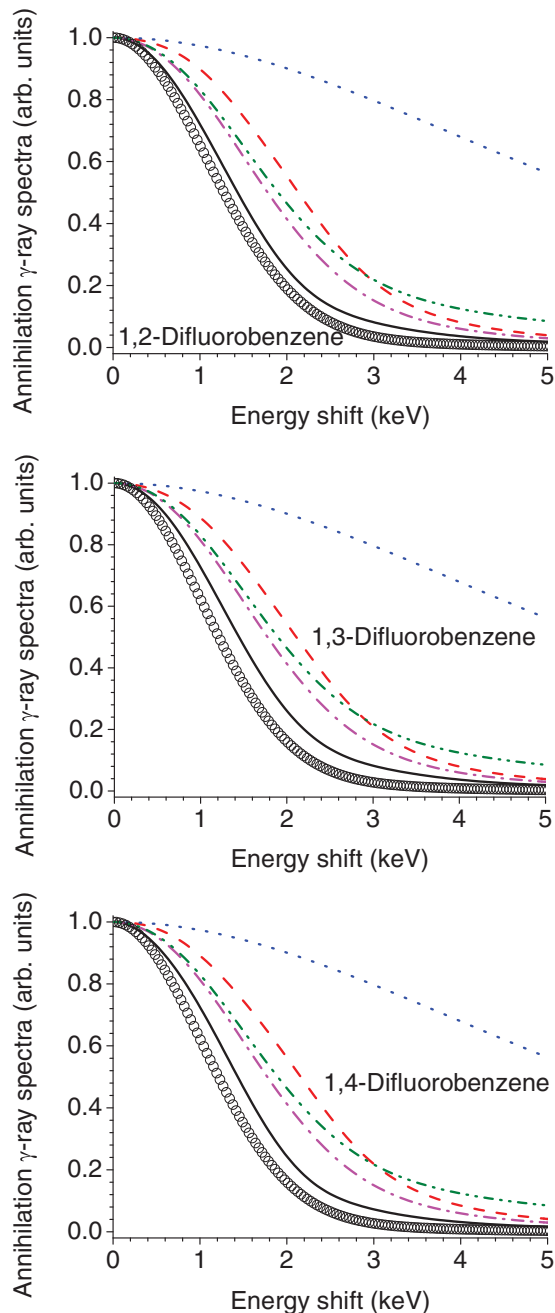


FIG. 22. Comparison of the theoretical γ -ray spectral profiles (lines) of 1,2-difluorobenzene, 1,3-difluorobenzene, and 1,4-difluorobenzene molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

with the same experiment. Among all the valence electrons, the agreement of the outer valence electrons is the worst one.

As one can see in Table III, for all the inner valence electrons, the composition of p electrons of atomic fluorine and carbon only contributes a little to the inner valence orbitals. Most of the inner valence electrons are composed by $2s$ electrons of atomic fluorine and carbon, and small parts of $1s$ electrons of hydrogen atoms. Especially for the LOVO orbital $8a'$, the $2s$ electrons of the fluorine atom contribute 90.4% in

the composition. This indicates that $2s$ electrons of the fluorine atom dominate this orbital. The inner valence electrons can be considered as s -like electrons, most of these electrons will distribute at the low-energy region.

The composition of outer valence electrons is also analyzed using the same method as shown in Table IV. In all these outer valence orbitals, there are almost no composition of $2s$ electrons of atomic fluorine and carbons. The $1s$ of the hydrogen atom also has a little contribution to the outer valence electrons, the same as to the inner valence electrons. The dominant contribution is from the $2p$ electrons of atomic carbons and fluorine. Hence, the outer valence electrons have the p -like behavior. The momentum of these outer valence electrons is distributed far away from the zero momentum. The widths of γ -ray spectra of these outer valence electrons are larger than the inner valence as shown in Fig. 18.

Figure 19 shows the theoretical Hirshfeld charges of 1-fluorohexane molecule. All the hydrogen atoms are positively charged and about 10% charges for each hydrogen atom have been attracted into the other ends, carbon atoms. The carbon atoms are negatively charged then except for the number six carbon C6. C6 is positively charged due to the strong attraction from fluorine atom. The maximum net charges are distributed at the both ends of 1-fluorohexane: C7 and F1 atoms. These two sites will be the most positrophilic sites in this molecule. The other carbon atoms, C5, C3, C2, and C4 are weakly negatively charged and also the positrophilic electrons. This also proves, on the other hand, that the positron will be attracted into these atoms in molecule and annihilates with the electrons around these atoms. As shown in Fig. 20, the electrons in molecules almost are distributed around atomic carbons and fluorine. The fluorine atom attracts more electrons than carbon atoms. In the hydrogen atoms, although they are the outermost atoms distributed in molecule, only parts of electrons from them have been attracted into carbon or fluorine atoms, the positive charge repulses positron approaching to the hydrogen atoms.

The annihilation process can be seen clearly from LMAP as shown in Fig. 21. The positrophilic sites can be represented by the positive LMAP. LMAP also shows why the outermost hydrogen atoms are not the positrophilic sites in 1-fluorohexane molecule. The positrophilic sites, as one can see, are distributed between the C-H bonds. This indicates that the incoming positron will be attracted into this area and annihilate with the electrons over there. The maximum of the positive LMAP region is around the fluorine atom. This means the fluorine atom has strong attraction for the positron. The fluorine atom in 1-fluorohexane would be the strong positrophilic region and the positron will annihilate mostly with the electrons in nearby fluorine atom. This also can be proven from Table III that most of the LOVO electrons are dominated by the $2s$ electrons of atomic fluorine and the inner valence electrons dominate the γ -ray spectra.

J. Fluorinated benzenes

The γ -ray spectra in benzene and its fluoroderivatives are found to be dominated by inner valence electrons too as shown in Fig. 22 and Fig. 23. The halogen atoms have most negative charges in these derivatives. The incoming positron will disturb

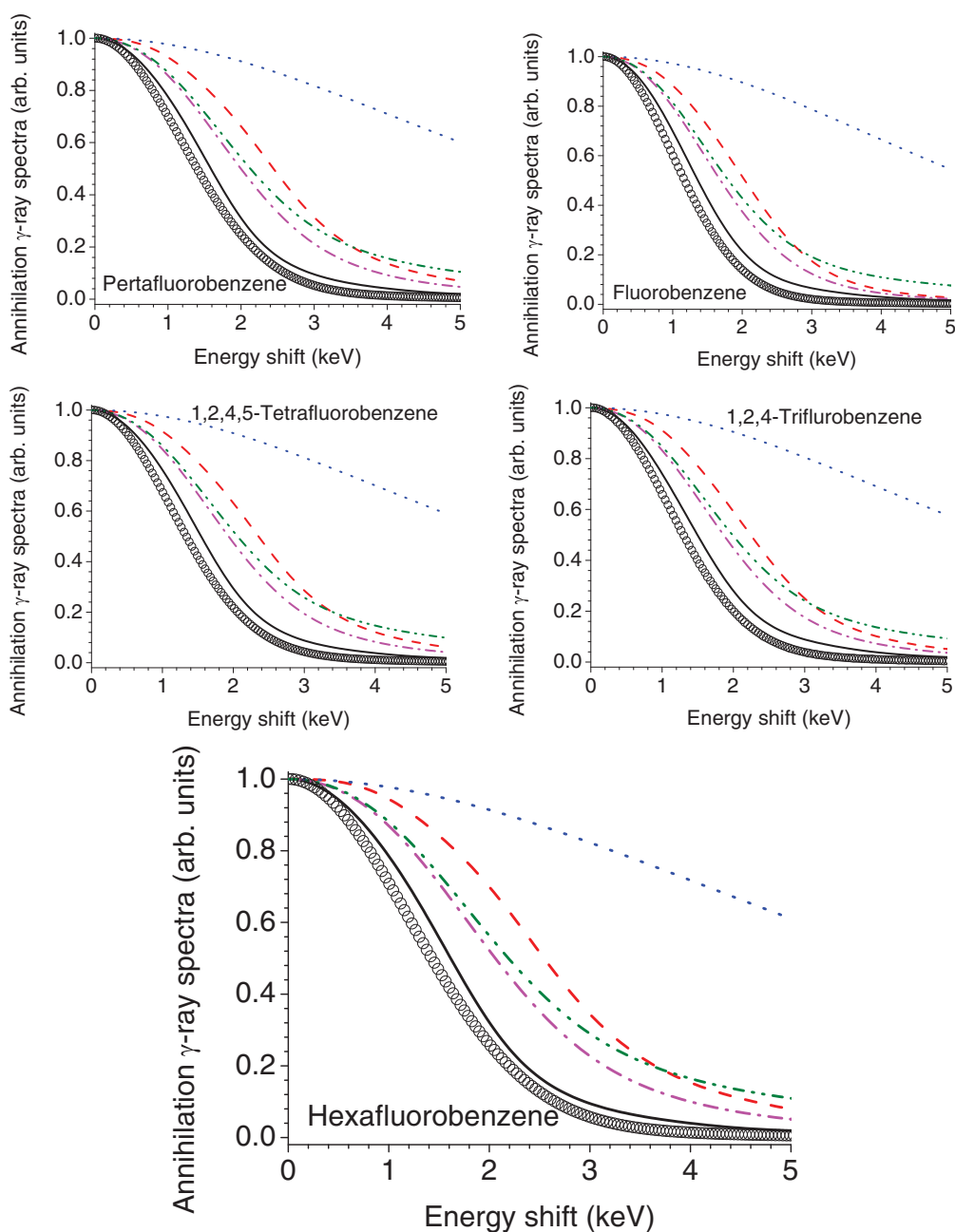


FIG. 23. Comparison of the theoretical γ -ray spectral profiles (lines) of 1,2,4-trifluorobenzene, 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, hexafluorobenzene, and fluorobenzene molecules in positron-electron annihilation process with two-Gaussian fitted experimental (circles) [12].

these net negative charges more easily. Hence, neglect of the positron effects will lead us to underestimate the contribution of these inner valence electrons [1]. The strong correlations from 99.23% to 99.70% of the inner valence electrons with experimental data are found. As a result, the inner valence electrons dominate the positron annihilating process under the low-energy positron wave function approximation and this is very interesting.

The γ -ray spectra are not sensitive to the chemical structures of molecules. The number of substituted fluorine atoms will be an important property in the γ -ray spectra rather than the substituted positions in difluorobenzenes. The information of the position or space effects have been canceled

in the single-center momentum distributions. The number of the substituted fluorine atoms will influence the γ -ray spectra strongly. In other words, fluorine atoms in these molecules are the positrophilic regions and the positron prefers to annihilate in this area. From one substitution of fluorine atoms to the full substitution in benzene, the width of γ -ray spectra increases from 2.39, to 2.46(2.61), 2.61, 2.66, 2.83, 2.91 keV gradually. This indicates the inner valence electrons are bound tightly more and more as the number of fluorine atoms increases. The comparison shows that the inner valence electrons have the special place in the positron-electron annihilation process and dominate the γ -ray spectra as proved for other molecules.

IV. CONCLUSIONS

The positron-electron annihilation γ -ray spectra of 64 molecules and atoms have been studied systematically. The theoretical orbital-dependent Doppler broadening γ -ray spectra for core, inner valence, and outer valence electrons of these molecules has been computed and compared with the corresponding experiments. Unexpectedly, the present results show that the positrons annihilate predominantly with the inner valence electrons, especially LOVO electrons rather than the outer valence electrons. The γ -ray profiles of the inner valence electrons have a strong correlation with the experimental results. These findings are interesting because it has been supposed to have larger probability for positrons annihilating with outer valence electrons rather than inner valence electrons.

The comparison of γ -ray spectra of these electrons with the total measurements of each molecule shows some interesting phenomena, which are not observed in previous studies. For all these molecules, core electrons show little contribution to the total γ -ray spectra as is well known. However, when the valence electrons are divided into inner valence and outer valence, the different behavior between these two kinds of valence electrons is found. In the annihilation process, although the outer valence, especially HOMO electrons, are the outermost valence electrons, they seem to have only little correlation with the positron annihilation probability. The inner valence electrons, especially LOVO electrons, have a strong correlation and good agreement with the total γ -ray spectra of molecules otherwise.

As is well known, in chemical reaction and scattering process, molecules and atoms lose the outermost electrons easily compared with other bound electrons due to the smallest bound energy. The inner valence electrons have larger bound energies than the outer valence electrons, so they can not easily be removed from molecules and atoms. Usually these physical processes can be expressed by some transition matrices where the energy dominator plays an important role. However, it seems that the inner valence electrons have more probabilities to annihilate with positron than the outer valence electrons. These unusual phenomena have been explained in the present work.

The electrons distributed in the lower momentum region play an important role in the γ -ray spectra under the low-energy plane-wave approximation. As is well known, the core electrons have the widest width compared to valence electrons and contribute only a little effects on the annihilation process. For all these molecules, the inner valence electrons are almost distributed in the lower momentum region, usually within the FWHM region, while the core and outer valence electrons are almost distributed out of the FWHM region. Accordingly, the γ -ray spectra of the inner valence electrons have the narrowest width compared to all other electrons. Hence, the inner valence electrons achieve an excellent agreement with the experimental measurements rather than outer valence electrons and core electrons.

The present work also suggests that the accurate positron wave functions must be involved to identify the dominance of the bound electrons clearly in positron-electron annihilation process. The electron and positron correlations must also be considered. This will require more accurate wave functions of the incoming positron to confirm the positrophilic electrons in further study.

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APPENDIX: GAMMA-RAY LINE WIDTHS AND CORRELATION COEFFICIENTS FOR CORE, INNER, AND OUTER VALENCE ELECTRONS OF 64 MOLECULES

Most of experiments only give the full width at half maximum (FWHM) of the profiles. In Table V, the FWHMs for different kinds of electrons are given and compared with the experimental measurements. In order to find out the correlation between the theoretical prediction and the experimental measurements, the correlation coefficient with the experimental results for each kind of electrons are listed in Table VI. The division of bound electrons is approximately due to the large energy gap between core, inner valence, and outer valence electrons. The electron configurations of all these electrons in all molecules are listed in Table VII.

TABLE V. The γ -ray line widths E (keV) of the different kinds of annihilated electrons for all the studied atoms and molecules in the present work. For comparison, the recent experimental values are also listed [12].

Molecule	Formula	Core	Outer valence	Valence	Total	Inner valence	Expt. [12]
Helium	He	–	–	–	3.06	–	2.31
Neon	Ne	17.82	5.89	5.00	5.22	3.58	3.28
Argon	Ar	13.35	3.80	3.36	3.95	2.46	2.31
Krypton	Kr	14.09	3.36	2.98	4.25	2.16	2.09
Xenon	Xe	11.48	2.83	2.54	4.40	1.86	1.86
Radon	Rn	–	2.76	2.54	–	1.94	–
Hydrogen	H ₂	–	–	–	2.09	–	1.64
Nitrogen	N ₂	12.30	3.65	3.36	3.58	3.13	2.16
Oxygen	O ₂	14.17	4.70	4.03	4.25	3.36	2.68
Carbon monoxide	CO	11.86	3.28	3.36	3.58	3.36	2.09
Carbon dioxide	CO ₂	12.45	4.40	3.88	4.10	3.28	2.61
Water	H ₂ O	14.17	4.25	3.73	3.80	2.68	2.54
Sulfur hexafluoride	SF ₆	13.35	5.37	4.47	4.85	3.28	2.98

TABLE V. (*Continued.*)

Molecule	Formula	Core	Outer valence	Valence	Total	Inner valence	Expt. [12]
Ammonia	NH ₃	12.30	3.73	3.21	3.36	2.31	2.24
Methanol	CH ₃ OH	11.86	3.95	3.36	3.58	2.54	2.54
Tetraethylsilane	Si(C ₂ H ₅) ₄	9.99	3.80	3.13	3.36	2.31	2.37
Nitrobenzene	C ₆ H ₅ NO ₂	11.18	4.25	3.50	3.73	2.83	2.47
Pyridine	C ₅ H ₅ N	10.66	4.03	3.28	3.50	2.68	2.31
Methane	CH ₄	10.44	3.43	2.91	2.98	2.01	2.09
Ethane	C ₂ H ₆	10.44	3.58	2.98	3.13	2.24	2.16
Propane	C ₃ H ₈	10.44	3.65	3.04	3.21	2.31	2.24
Butane	C ₄ H ₁₀	10.44	3.73	3.06	3.21	2.31	2.31
Pentane	C ₅ H ₁₂	10.44	3.73	3.13	3.28	2.31	2.24
Hexane	C ₆ H ₁₄	10.44	3.73	3.13	3.28	2.31	2.24
Heptane	C ₇ H ₁₆	10.44	3.80	3.13	3.28	2.39	–
Octane	C ₈ H ₁₈	10.44	3.80	3.13	3.28	2.39	–
Nonane	C ₉ H ₂₀	10.44	3.80	3.13	3.28	2.39	2.31
Decane	C ₁₀ H ₂₂	10.44	3.80	3.13	3.28	2.39	–
Undecane	C ₁₁ H ₂₄	10.44	3.80	3.13	3.28	2.39	–
Dodecane	C ₁₂ H ₂₆	10.44	3.88	3.13	3.36	2.39	2.31
Cyclohexane	C ₆ H ₁₂	10.44	3.88	3.21	3.36	2.46	2.31
2-Methylbutane	C ₅ H ₁₂	10.44	3.73	3.13	3.28	2.31	2.24
2,2-Dimethylpropane	C(CH ₃) ₄	10.44	3.73	3.13	3.28	2.31	2.24
Ethylene	C ₂ H ₄	10.44	3.65	3.06	3.21	2.39	2.09
Acetylene	C ₂ H ₂	10.44	3.50	2.98	3.21	2.54	2.09
Benzene	C ₆ H ₆	15.66	4.03	3.21	3.43	2.61	2.24
Naphthalene	C ₁₀ H ₈	10.44	4.10	3.28	3.50	2.68	2.31
Anthracene	C ₁₄ H ₁₀	10.44	4.18	3.28	3.50	2.76	2.46
Toluene	C ₆ H ₅ CH ₃	10.44	3.95	3.21	3.43	2.61	2.31
Carbon tetrafluoride	CF ₄	14.17	5.52	4.55	4.77	3.43	2.98
Carbon tetrachloride	CCl ₄	12.23	3.80	3.21	3.80	2.46	2.31
Carbon tetrabromide	CBr ₄	13.27	3.43	2.98	4.18	2.31	2.09
Methyl fluoride	CH ₃ F	12.23	4.18	3.58	3.73	2.68	2.68
Difluoromethane	CH ₂ F ₂	13.20	4.70	4.03	4.25	3.13	2.76
Trifluoromethane	CHF ₃	13.79	5.14	4.32	4.55	3.36	2.76
Fluoroethane	C ₂ H ₅ F	11.48	4.03	3.43	3.58	2.61	2.54
1,1,1-Trifluoroethane	CF ₃ CH ₃	12.82	4.70	3.95	4.18	3.06	2.83
1,1,2-Trifluoroethane	CHF ₂ CH ₂ F	12.82	4.77	4.03	4.25	3.06	2.83
1,1,1,2-Tetrafluoroethane	CF ₃ CH ₂ F	13.20	5.00	4.18	4.40	3.21	2.91
1,1,2,2-Tetrafluoroethane	CHF ₂ CHF ₂	13.20	5.07	4.18	4.40	3.21	2.91
Hexafluoroethane	C ₂ F ₆	13.79	5.44	4.47	4.70	3.36	2.98
2,2-Difluoropropane	CH ₃ CF ₂ CH ₃	11.78	4.25	3.58	3.73	2.68	2.68
1,1,1-Trifluoropropane	CF ₃ C ₂ H ₅	12.23	4.47	3.80	3.95	2.91	2.76
Perfluoropropane	C ₃ F ₈	13.64	5.44	4.47	4.70	3.36	2.98
1-Fluorohexane	CH ₂ FC ₅ H ₁₁	10.81	3.95	3.28	3.43	2.46	2.46
Perfluorohexane	C ₆ F ₁₄	13.42	5.44	4.40	4.70	3.36	3.06
Fluorobenzene	C ₆ H ₅ F	10.81	4.10	3.43	3.65	2.76	2.39
1,2-Difluorobenzene	C ₆ H ₄ F ₂	11.18	4.32	3.58	3.80	2.91	2.61
1,3-Difluorobenzene	C ₆ H ₄ F ₂	11.18	4.25	3.58	3.80	2.91	2.46
1,4-Difluorobenzene	C ₆ H ₄ F ₂	11.18	4.32	3.58	3.80	2.91	2.46
1,2,4-Trifluorobenzene	C ₆ H ₃ F ₃	11.48	4.55	3.73	4.03	3.06	2.61
1,2,4,5-Tetrafluorobenzene	C ₆ H ₂ F ₄	11.78	4.77	3.88	4.18	3.13	2.68
Pentafluorobenzene	C ₆ HF ₅	12.00	4.92	4.03	4.32	3.21	2.83
Hexafluorobenzene	C ₆ F ₆	12.23	5.14	4.18	4.40	3.28	2.91

TABLE VI. The γ -ray line-shape correlation coefficients (%) with the two-Gaussian fitted experiments [12] of the different kinds of annihilated electrons for all the studied atoms and molecules in the present work.

Molecule	Formula	Core	Inner valence	Outer Valence	Valence	Total
Helium	He	–	–	–	–	98.11
Neon	Ne	59.54	99.68	92.02	95.33	93.70
Argon	Ar	57.18	99.72	94.41	96.63	89.35
Krypton	Kr	52.93	99.74	95.27	97.13	79.81
Xenon	Xe	54.91	99.78	96.55	98.09	76.45
Radon	Rn	–	–	–	–	–
Hydrogen	H ₂	–	–	–	–	98.11
Nitrogen	N ₂	59.47	97.34	93.78	95.57	93.03
Oxygen	O ₂	60.32	98.93	92.79	95.78	93.71
Carbon monoxide	CO	59.64	94.82	94.47	94.64	91.94
Carbon dioxide	CO ₂	62.96	98.67	93.71	96.17	93.91
Water	H ₂ O	58.93	99.81	94.06	96.52	95.14
Sulfur hexafluoride	SF ₆	65.07	99.81	92.52	96.17	93.41
Ammonia	NH ₃	59.14	99.87	94.21	96.67	95.39
Methanol	CH ₃ OH	64.28	99.98	95.80	98.00	96.65
Tetraethylsilane	Si(C ₂ H ₅) ₄	–	–	–	–	–
Nitrobenzene	C ₆ H ₅ NO ₂	–	–	–	–	–
Pyridine	C ₅ H ₅ N	64.12	99.54	93.67	97.11	94.97
Methane	CH ₄	61.71	99.96	94.80	97.39	96.18
Ethane	C ₂ H ₆	62.77	99.98	94.93	97.61	96.24
Propane	C ₃ H ₈	63.19	99.97	94.76	97.60	96.16
Butane	C ₄ H ₁₀	64.61	99.98	95.27	98.02	96.66
Pentane	C ₅ H ₁₂	63.67	99.97	94.62	97.64	96.15
Hexane	C ₆ H ₁₄	63.79	99.96	94.59	97.66	96.15
Heptane	C ₇ H ₁₆	–	–	–	–	–
Octane	C ₈ H ₁₈	–	–	–	–	–
Nonane	C ₉ H ₂₀	64.97	99.97	94.94	97.97	96.52
Decane	C ₁₀ H ₂₂	–	–	–	–	–
Undecane	C ₁₁ H ₂₄	–	–	–	–	–
Dodecane	C ₁₂ H ₂₆	64.41	99.96	94.60	97.78	96.25
Cyclohexane	C ₆ H ₁₂	64.79	99.94	94.53	97.69	96.14
2-Methylbutane	C ₅ H ₁₂	63.42	99.96	94.22	97.44	95.91
2,2-Dimethylpropane	C(CH ₃) ₄	63.65	99.98	94.54	97.63	96.12
Ethylene	C ₂ H ₄	61.94	99.63	93.58	96.69	94.84
Acetylene	C ₂ H ₂	61.58	98.95	93.72	96.52	94.16
Benzene	C ₆ H ₆	63.54	99.53	93.05	96.87	94.69
Naphthalene	C ₁₀ H ₈	64.48	99.52	93.43	97.12	94.91
Anthracene	C ₁₄ H ₁₀	66.20	99.77	94.51	97.88	95.80
Toluene	C ₆ H ₅ CH ₃	64.43	99.70	93.86	97.31	95.32
Carbon tetrafluoride	CF ₄	63.26	99.48	91.92	95.67	93.75
Carbon tetrachloride	CCl ₄	59.81	99.80	94.86	97.36	90.37
Carbon tetrabromide	CBr ₄	54.29	99.74	95.00	97.32	80.36
Methyl fluoride	CH ₃ F	64.72	99.94	95.67	97.82	96.33
Difluoromethane	CH ₂ F ₂	63.51	99.66	93.63	96.55	94.79
Trifluoromethane	CHF ₃	62.08	99.16	91.51	95.14	93.19
Fluoroethane	C ₂ H ₅ F	65.14	99.96	95.58	97.91	96.40
1,1,1-Trifluoroethane	CF ₃ CH ₃	65.29	99.86	94.61	97.33	95.60
1,1,2-Trifluoroethane	CHF ₂ CH ₂ F	65.02	99.84	94.08	97.08	95.32
1,1,1,2-Tetrafluoroethane	CF ₃ CH ₂ F	64.91	99.79	93.63	96.83	95.02
1,1,2,2-Tetrafluoroethane	CHF ₂ CHF ₂	64.66	99.77	93.23	96.64	94.81
Hexafluoroethane	C ₂ F ₆	64.04	99.65	92.14	96.04	94.12
2,2-Difluoropropane	CH ₃ CF ₂ CH ₃	65.88	99.94	95.54	97.92	96.33
1,1,1-Trifluoropropane	CF ₃ C ₂ H ₅	65.65	99.90	94.93	97.57	95.88
Perfluoropropane	C ₃ F ₈	64.52	99.72	92.29	96.25	94.32

TABLE VI. (Continued.)

Molecule	Formula	Core	Inner valence	Outer Valence	Valence	Total
1-Fluorohexane	CH ₂ FC ₅ H ₁₁	65.06	99.97	95.00	97.88	96.33
Perfluorohexane	C ₆ F ₁₄	65.32	99.82	92.65	96.60	94.69
Fluorobenzene	C ₆ H ₅ F	64.64	99.44	93.81	96.93	94.75
1,2-Difluorobenzene	C ₆ H ₄ F ₂	66.35	99.63	94.69	97.44	95.37
1,3-Difluorobenzene	C ₆ H ₄ F ₂	64.89	99.23	93.76	96.65	94.45
1,4-Difluorobenzene	C ₆ H ₄ F ₂	64.85	99.39	93.33	96.68	94.45
1,2,4-Trifluorobenzene	C ₆ H ₃ F ₃	65.99	99.51	93.94	96.98	94.85
1,2,4,5-Tetrafluorobenzene	C ₆ H ₂ F ₄	66.03	99.55	93.40	96.83	94.68
Pentafluorobenzene	C ₆ HF ₅	66.66	99.66	93.53	97.00	94.90
Hexafluorobenzene	C ₆ F ₆	66.65	99.70	93.01	96.86	94.77

TABLE VII. The electron configurations for the core, inner valence, and outer valence orbitals for all the studied atoms and molecules in the present work. The orbitals in bold are LOVO and HOMO, respectively.

Molecule (Formula)	Core	Inner valence	Outer valence
Helium (He)		<i>a</i>1a²	
Neon (Ne)	1a ² _{1g}	2a²_{1g}	1t⁶_{1u}
Argon (Ar)	1a ² _{1g} -1t ⁶ _{1u}	3a²_{1g}	2t⁶_{1u}
Krypton (Kr)	1a ² _{1g} -1e ⁴ _g	4a²_{1g}	3t⁶_{1u}
Xenon (Xe)	1a ² _{1g} -2t ⁶ _{2g}	5a²_{1g}	4t⁶_{1u}
Radon (Rn)	–	6a²_{1g}	5t⁶_{1u}
Hydrogen (H ₂)		1σ²_g	
Nitrogen (N ₂)	1σ ² _g 1σ ² _u	2σ²_g2σ²_u	3σ ² _g 1π ⁴ _u
Oxygen (O ₂)	1σ ² _g 1σ ² _u	2σ²_g2σ²_u	1π ⁴ _u -1π ² _g
Carbon monoxide (CO)	1σ ² _g 2σ ² _g	3σ²_g4σ²_g	1π ⁴ 5σ ² _g
Carbon dioxide (CO ₂)	1σ ² _u -2σ ² _g	3σ²_g-4σ²_g	3σ ² _u -1π ⁴ _g
Water (H ₂ O)	1a ² ₁	2a²₁	1b ² ₂ -1b ² ₁
Sulfur hexafluoride (SF ₆)	1a ² _{1g} -1t ⁶ _{1u}	4a²_{1g}-5a²_{1g}	4t ⁶ _{1u} -1t ⁶ _{1g}
Ammonia (NH ₃)	1a ²	2a²	3a ² -5a ²
Methanol (CH ₃ OH)	1a ² 2a ²	3a²4a²	5a ² -2a ² '
Tetraethylsilane (Si(C ₂ H ₅) ₄)	1a ² -13a ²	14a²-22a²	23a ² -41a ²
Nitrobenzene (C ₆ H ₅ NO ₂)	1a ² -9a ²	10a²-18a²	1a ² '-5a ² '
Pyridine (C ₅ H ₅ N)	1a ² -6a ²	7a²-12a²	13a ² -3a ² '
Methane (CH ₄)	1a ²	2a²	3t⁶
Ethane (C ₂ H ₆)	1a ² _g 1b ² _u	2a²_g2b²_u	3b ² _u -1b ² _g
Butane (C ₃ H ₈)	1a ² ₁ -2a ² ₁	3a²₁-4a²₁	1b ² ₂ -2b ² ₁
Butane (C ₄ H ₁₀)	1a ² _g -2b ² _u	3a²_g-4b²_u	1a ² _u -2b ² _g
Pentane (C ₅ H ₁₂)	1a ² ₁ -3a ² ₁	4a²₁-6a²₁	1b ² ₁ -7b ² ₂
Hexane (C ₆ H ₁₄)	1a ² _g -3b ² _u	4a²_g-6b²_u	1a ² _u -10a ² _g
Heptane (C ₇ H ₁₆)	1a ² '-7a ²	8a²'-14a²	1a ² '-22a ² '
Octane (C ₈ H ₁₈)	1a ² _g -4b ² _u	5a²_g-8b²_u	1a ² _u -13a ² _g
Nonane (C ₉ H ₂₀)	1a ² '-9a ²	10a²'-18a²	1a ² '-28a ² '
Decane (C ₁₀ H ₂₂)	1a ² _g -5b ² _u	6a²_g-10b²_u	1a ² _u -16a ² _g
Undecane (C ₁₁ H ₂₄)	1a ² '-11a ²	12a²'-22a²	1a ² '-34a ² '
Dodecane (C ₁₂ H ₂₆)	1a ² _g -6b ² _u	7a²_g-12b²_u	1a ² _u -19a ² _g
Cyclohexane (C ₆ H ₁₂)	1a ² -6a ²	7a²-12a²	13a ² -24a ²
2-Methylbutane (C ₅ H ₁₂)	1a ² -5a ²	6a²-10a²	11a ² -21a ²
2,2-Dimethylpropane (C ₅ H ₁₂)	1a ² -4a ²	5a²-8a²	9a ² -7a ² '

TABLE VII. (Continued.)

Molecule (Formula)	Core	Inner valence	Outer valence
Ethylene (C ₂ H ₄)	$1a_g^2 1b_{1u}^2$	$2a_g^2 2b_{1u}^2$	$1b_{2u}^2 - 1b_{3u}^2$
Acetylene (C ₂ H ₂)	$1\sigma_g^2 1\sigma_u^2$	$2\sigma_g^2 2\sigma_u^2$	$3\sigma_g^2 1\pi_u^4$
Benzene (C ₆ H ₆)	$1a_{1g}^2 - 1b_{1u}^2$	$2a_{1g}^2 - 3a_{1g}^2$	$2b_{1u}^2 - 1e_{1g}^4$
Naphthalene (C ₁₀ H ₈)	$1a_g^2 - 3b_{1u}^2$	$4a_g^2 - 5b_{2u}^2$	$7a_g^2 - 1a_u^2$
Anthracene (C ₁₄ H ₁₀)	$1a_g^2 - 4b_{1u}^2$	$5a_g^2 - 9a_g^2$	$6b_{3g}^2 - 2b_{2g}^2$
Toluene (C ₆ H ₅ CH ₃)	$1a'^2 - 7a'^2$	$8a'^2 - 14a'^2$	$15a'^2 - 4a''^2$
Carbon tetrafluoride (CF ₄)	$1t_1^6 - 2a_1^2$	$3a_1^2 - 4a_1^2$	$3t_2^6 - 1t_1^6$
Carbon tetrachloride (CCl ₄)	$1a'^2 - 14a'^2$	$15a'^2 - 18a'^2$	$19a'^2 - 13a''^2$
Carbon tetrabromide (CBr ₄)	$1a'^2 - 35a'^2$	$36a'^2 - 39a'^2$	$24a''^2 - 45a''^2$
Methyl fluoride (CH ₃ F)	$1a'^2 2a'^2$	$3a'^2 4a'^2$	$1a''^2 - 7a''^2$
Difluoromethane (CH ₂ F ₂)	$1a'^2 - 3a'^2$	$4a'^2 - 6a'^2$	$1a''^2 - 3a''^2$
Trifluoromethane (CHF ₃)	$1e^4 - 2a_1^2$	$3a_1^2 - 4a_1^2$	$5a_1^2 - 6a_1^2$
Fluoroethane (C ₂ H ₅ F)	$1a'^2 - 3a'^2$	$4a'^2 - 6a'^2$	$1a''^2 - 3a''^2$
1,1,1-Trifluoroethane (CF ₃ CH ₃)	$1a''^2 - 3a'^2$	$4a'^2 - 6a'^2$	$7a'^2 - 14a'^2$
1,1,2-Trifluoroethane (CHF ₂ CH ₂ F)	$1a'^2 - 5a'^2$	$6a'^2 - 10a'^2$	$11a'^2 - 21a'^2$
1,1,1,2-Tetrafluoroethane (CF ₃ CH ₂ F)	$1a'^2 - 5a'^2$	$6a'^2 - 10a'^2$	$3a''^2 - 17a''^2$
1,1,2,2-Tetrafluoroethane (CHF ₂ CHF ₂)	$1a_g^2 - 3a_u^2$	$4a_g^2 - 6a_u^2$	$7a_u^2 - 13a_g^2$
Hexafluoroethane (C ₂ F ₆)	$1a_g^2 - 3b_u^2$	$4a_g^2 - 6b_u^2$	$7a_g^2 - 11a_g^2$
2,2-Difluoropropane (CH ₃ CF ₂ CH ₃)	$1a'^2 - 4a'^2$	$5a'^2 - 8a'^2$	$9a'^2 - 7a''^2$
1,1,1-Trifluoropropane (CF ₃ C ₂ H ₅)	$1a''^2 - 5a'^2$	$6a'^2 - 10a'^2$	$3a''^2 - 8a''^2$
Perfluoropropane (C ₃ F ₈)	$1a''^2 - 8a'^2$	$9a'^2 - 16a'^2$	$17a'^2 - 28a''^2$
1-Fluorohexane (CH ₂ FC ₅ H ₁₁)	$1a'^2 - 7a'^2$	$8a'^2 - 14a'^2$	$1a''^2 - 22a''^2$
Perfluorohexane (C ₆ F ₁₄)	$1b_g^2 - 7b_u^2$	$8a_g^2 - 14b_u^2$	$15b_u^2 - 25a_g^2$
Fluorobenzene (C ₆ H ₅ F)	$1a'^2 - 7a'^2$	$8a'^2 - 14a'^2$	$15a'^2 - 4a''^2$
1,2-Difluorobenzene (C ₆ H ₄ F ₂)	$1b_2^2 - 4b_2^2$	$5a_1^2 - 9a_1^2$	$8b_2^2 - 3b_1^2$
1,3-Difluorobenzene (C ₆ H ₄ F ₂)	$1a'^2 - 8a'^2$	$9a'^2 - 16a'^2$	$17a'^2 - 29a'^2$
1,4-Difluorobenzene (C ₆ H ₄ F ₂)	$1a'^2 - 8a'^2$	$9a'^2 - 16a'^2$	$17a'^2 - 29a'^2$
1,2,4-Trifluorobenzene (C ₆ H ₃ F ₃)	$1a'^2 - 9a'^2$	$10a'^2 - 18a'^2$	$19a'^2 - 6a''^2$
1,2,4,5-Tetrafluorobenzene (C ₆ H ₂ F ₄)	$1a'^2 - 10a'^2$	$11a'^2 - 20a'^2$	$21a'^2 - 37a'^2$
Pentafluorobenzene (C ₆ HF ₅)	$1a'^2 - 11a'^2$	$12a'^2 - 22a'^2$	$23a'^2 - 8a''^2$
Hexafluorobenzene (C ₆ F ₆)	$1a'^2 - 12a'^2$	$13a'^2 - 24a'^2$	$25a'^2 - 45a'^2$

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