Double ionization of fluorinated benzenes: Hole localization and delocalization effects

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(Received 24 July 2003; accepted 28 October 2003)

The dense double ionization spectra of all the twelve fluoro-substituted benzene molecules are investigated in great detail by Green’s function ADC(2) calculations and a two-hole density mapping. Double ionization is shown to provide an extremely sensitive tool of electronic structure analysis. The calculations evidence and measure quantitatively how the charge distribution is dictated by the complex interplay between the resilience of the aromatic ring electronic structure and the disruptive effect of the electronegative halogen substituents. Successive substitutions are found not to have any synergic effect, but affect the spectra in very identifiable ways. The Auger spectra of the fluorobenzenes are interpreted in the light of the charge distribution results, using the foreign-imaging model. The double charge transfer spectra are also analyzed and discussed. © 2004 American Institute of Physics.

I. INTRODUCTION

There are 12 stable fluorine substituted benzene molecules—including isomers differing for the relative position of the substituents—and the doubly ionized states of a number of them, as well as of benzene itself, have been experimentally studied by several techniques. Among these, Auger electron spectra were measured for benzene6 and several fluorobenzenes.3 For those two molecules, lying at opposite ends of the substitution progression, fragmentation patterns of the dications were studied via several coincidence techniques (see, for example, Refs. 4, 5, and references therein). Double charge transfer (DCT) spectra of benzene6 and several fluorobenzenes3,7,8 were also measured.

The reason for this experimental interest lies, of course, in the fact that the study of physical processes on a series of related molecules is in general a very powerful tool to understand their electronic structure and chemistry, because comparing effects and trends as a function of the chemical environment is often extremely insightful. Double ionization, however, is a complicated process and the observable spectra are generally hard to understand in detail—except perhaps at the threshold—mainly because they are very dense: many electronic states contribute and a meaningful picture of their changing nature and energy in related systems is very difficult to obtain—impossible, in fact, without sound theoretical guidance. As a result, the double ionization spectra of fluorobenzenes were, for example, just described as being “remarkably similar.”7 Calculations at very simple levels of theory on some of the doubly ionized states of fluorobenzenes were actually carried out to accompany the experimental work,3,8,9 but the analysis was often limited, where at all possible, to a rather uninformative comparison between the observed peaks and the computed double ionization energies (DIE).

Double ionization processes, and especially the electronic rearrangement that accompanies them, are on the other hand sensitive and informative probes of the electronic structure. In this light, in the present work we have studied in great detail by accurate theoretical calculations the complete valence double ionization spectra and, in particular, the two-hole density distribution as a function of energy of all the fluorobenzene molecules. The attempt was to achieve a consistent picture of the charge transfer and screening processes along the whole series which would cast light on the changes in electronic structure induced by the halogen substituents, besides enabling a thorough understanding of the experimentally measured spectra. We have tried to interpret the theoretical results in terms of the alterations to the aromatic structure of the benzene ring caused by the electronegative substituents and—in so far as possible—give a quantitative measure of the strength of these effects. The interplay between aromatic character and halogen addition, which takes place through hole localization and delocalization effects, leaves fingerprinting marks on the spectra which we have tried to decrypt and understand qualitatively in general terms.

As mentioned above, the calculation of double ionization spectra is very demanding and requires the ability to balance the computation of a vast number of electronic states with the necessity to account, at least qualitatively, for electron correlation. The second order Green’s function method known as algebraic diagrammatic construction,10 implemented in a direct algorithm and coupled to the block-Lanczos iterative diagonalization, is known to provide such balance (see, for example, Ref. 11, and references therein) and is entirely adequate to describe the hole delocalization/localization effects which are the main subject of our study. The complete mapping of the double charge distribution, a

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key ingredient of the present work, has been carried out using a two-hole population analysis scheme.12

II. COMPUTATIONAL DETAILS

For the investigation of the simultaneous double ionization of an $N$-electron system we study the retarded part of the particle-particle propagator using the second order algebraic diagrammatic construction, ADC(2), method.10 This is a powerful direct approach for the theoretical study of ionization processes, leading to a sparse symmetric eigenvalue problem in the space of the ionic configurations, represented in the basis of the Hartree–Fock orbitals of the neutral system. The eigenvalues of the system are the ionization energies, while the eigenvectors are related to the spectroscopic amplitudes. For double ionization, the ADC(2) configuration space comprises all the two-hole (2h) configurations and their three-hole-one-particle single excitations (3h1p). The matrix elements in the main space are of second order in the electron repulsion and of first order in the remaining space. Therefore, the ADC eigensolutions provide results which are accurate beyond second order with respect to the naked 2h configurations, and beyond first order for the satellite excitations. This is essentially equivalent to ionized state energies obtained by configuration interaction including also the vast space of 4h2p configurations.10 The ADC(2) method is implemented in a direct integral-driven algorithm13 coupled to a block-Lanczos iterative diagonalizer11 which provides fast convergence onto the spectral envelope of the main space eigenvector projection, even when individual eigenvectors are not fully converged.14

Our Green’s functions calculations have been carried out on benzene, monofluorobenzene, the three difluorobenzenes, the three trifluorobenzenes, the three tetrafluorobenzenes, pentafluorobenzene, and hexafluorobenzene. For all molecules the Hartree–Fock preliminary calculations have been performed with the GAMESS-UK program15 using a contracted Gaussian double zeta16 plus polarization17 basis set. Experimental bond lengths and angles18 have been used in the calculations. These geometries retain the conventional symmetries of substituted benzenes. Benzene itself is a $D_{6h}$ molecule, C$_6$H$_5$F, ortho- and meta-C$_6$H$_4$F$_2$, and 1,2,3-C$_6$H$_4$F$_3$ are $C_{2v}$, para-C$_6$H$_4$F$_2$ is $D_{2h}$, 1,3,5-C$_6$H$_3$F$_3$ is $D_{3h}$ and 1,2,4-C$_6$H$_3$F$_3$ is $C_s$. The symmetry of the remaining systems is obtained from the above by exchanging H with F atoms. For each molecule, we obtained full convergence for all the eigenstates up to about 60 eV. At higher energies we ensured that the convolutions of the double ionization spectra which we shall discuss in the paper were also converged. In all cases we computed state densities of up to hundreds of states per eV. The size of the ADC matrices, after the obvious symmetry and spin factorization, were up to about half a million for the lower symmetry systems. Unless stated otherwise, to present a consistent view of the double ionization spectra, which is also easy to visualize and discuss, we adopt the device of showing figures with the relevant broadened convolutions of the computed doubly ionized states, where each state is assigned a Gaussian shape of full-width-at-half-maximum (FWHM) of 1 eV.

FIG. 1. (Color) Computed double ionization spectra of selected fluorobenzenes obtained by Gaussian convolution of the 2h weight of the discrete states (FWHM 1 eV). The blue shaded area is the benzene spectrum, the green one is the monofluorobenzene spectrum.
III. OVERVIEW OF THE DOUBLE IONIZATION SPECTRA

In Fig. 1 we report an overview of the computed double ionization spectra of selected fluorobenzenes, shown as broadened distributions of the 2h components (the spectra of benzene and monofluorobenzene are shown as shaded areas). For simplicity, only one spectrum is shown of each isomer having the same number of fluorine substituents. The computed double ionization spectra are very dense, containing between 10 and 30 thousand states (increasing with the number of fluorine atoms from 2 to 6) with 2h weight larger than 0.01 in the energy range shown. Benzene and monofluorobenzene have somewhat less crowded spectra, with about 2000 and 6500 states, respectively. While there are few isolated states just above the double ionization threshold, the density of states increases sharply at higher energy, until it mimics the background triple ionization continuum, with up to hundreds of states per eV. To make sense of such dense spectra, we have to start by extracting global information, such as is presented in the figure.

All the spectra show a similar overall structure, with a broad and intense distribution at low energy below about 55 eV, more or less distinctly separated from a second intense structure centered at about 60 eV and further weaker bands at higher energy. Such second feature, however, appears to be strictly connected to the presence of more than one fluorine atoms, since it is virtually absent in benzene and monofluorobenzene, and sharply gains strength for higher substitution levels. The similarities among the spectra do no stop here and even some evident substructures of the main regions of intensity are common to nearly all molecules, such as the two distinct bands between 40 and 50 eV. However, all these features are the result of literally thousands of individual transitions with very low 2h weight and it is hopeless to try to understand them without some more powerful global tool of analysis. The high energy features, between 70 and 100 eV are also remarkably similar in all the spectra, differing clearly in intensity and, above all, for an evident shift towards higher energies with increasing number of fluorine atoms. Such an increase in ionization energy is common to many features over the whole spectrum and reflects the electronic stabilization induced by the fluorines.

As we mentioned above, in the lowest energy region around 25 eV one can observe three or four well-isolated transitions which give rise to a first small peak at the extreme left of the spectrum. For all molecules, the 2h configurations that essentially describe these transitions are mainly double ionizations of the two highest occupied molecular orbitals. The electron density associated to these orbitals is in all cases mainly located on the carbon ring, its spatial distribution reflecting the symmetry of the out of plane atomic p functions. This makes the double ionization threshold for all molecules in the series remarkably invariant. The computed values (presumably somewhat underestimated because of a corresponding underestimation of ground state correlation) are 23.4 for benzene, 23.7 eV for monofluorobenzene, 23.8–24.1 eV for the difluorobenzenes, 24.4–24.5 eV for the trifluorobenzenes, 24.6–24.9 eV for the tetrafluorobenzenes, 25.2 eV for pentafluorobenzene, and 24.9 for hexafluorobenzene. For all molecules, only a handful of doubly ionized final states (mainly located in the lowest energy region) can be essentially described by a single 2h transition. For all the others, strong configuration mixing occurs.

IV. POPULATION ANALYSIS

As a consequence of the enormous number of states and of the strong correlation effects involved, unraveling the nature and patterns of the double ionization spectra seems complicated. As discussed above, the only fact we can easily state by inspection of the eigenvectors is that only a few states in the lowest energy region of the spectra of all the fluorinated benzenes are essentially described by a single 2h transition, and these represent the ionization of two delocalized orbitals on the aromatic ring.

To make progress, we need some way to extract concisely and usefully the essential information from the large amount of data contained in the double ionization spectra of all the molecules. Our work can be much simplified by looking at the results in terms of the probability density for the distribution of the two electron vacancies in the ionized states, which, in turn, can be usefully summarized in terms of the competition between different kinds of hole localization. To this purpose, we use a two-hole population analysis, as originally proposed in Ref. 12. This decomposes the 2h fraction of each eigenstate in partial contributions located on the various pairs of atomic centers. This gives a very helpful picture to understand the double charge distribution. We shall denote as C−1F−1, for example, a 2h component which represents the fraction of the charge distribution where one hole is localized on one carbon atom and the other hole on one fluorine atom. We can analyze such components individually for each given CF atom pair, studying for example how they change with the relative position and chemical environment of the selected carbon and fluorine atoms. Or we can sum them over all CF atom pairs, obtaining an overall estimate of the probability for having one hole located on any of the carbon atoms and the other on any of the fluorines. Similarly, we can study double charge components of X−1X−1 type, where one hole is located on one atom of type X (X=C, F, or H) and the second hole is localized on a different atom of the same type. The components we have mentioned are two-site components, representing hole localization of two different atoms. Then we also have components of the X−2 type, representing the probability for both holes to be localized on a single atom of type X (again, either one particular atom or the sum over a group of atoms of the same type). These are called one-site components. It is evident that, in principle, a great deal of insight can be gained on the nature of the doubly ionized states, in relation to their energy distribution, by studying in this way the charge density.

As an overview of the kind of information which can be extracted from the population analysis, we report in Fig. 2 and Fig. 3 the decomposition of the total 2h fraction in its partial components for benzene and six selected fluorobenzenes, shown as a convolution of the individual state populations. Only one isomer is reported for each of the di-, tri-, and tetra-substituted molecules, for the differences in the spectra of isomers are very small compared to those between...
systems with different number of halogen atoms. Furthermore, the $2h$ components involving hydrogen atoms have been omitted for clarity, since they are very small compared to the others. Only the summed components of a given type are plotted, without distinction for the different contributions of individual atom pairs. All the panels of both figures are on the same vertical scale, which makes very evident the enormous changes occurring as the number of fluorine substituents varies. Understanding the main features of the components is definitely easier than tackling the whole picture and offers immediately some extremely useful and general guidelines for the analysis. We may first of all differentiate between the one-site components, where both holes are located on the same atom, and two-site components. The former, shown as shaded areas in the figures, are generally much smaller than the other components, both because valence electrons are mostly shared in chemical bond regions and because the repulsion between two charges confined to a small region around one atomic center makes such situation energetically unfavorable. Nonetheless, we see that for the highest substituted species, the $F^{-2}$ component (green area) is quite significant in some four localized and well separated regions of the energy spectrum and may even dominate at high energy. The $C^{-2}$ component (blue area) shows by contrast a totally different distribution, spread over a wide region (especially the outer valence half) of the spectrum in the same way for all molecules, and everywhere very small.

The two-site components have one common area of large intensity below 50 eV. At higher energy, essentially only the $C^{-1}F^{-1}$ and $F^{-1}F'^{-1}$ components are significant, especially in the region between 55 and 70 eV, where the second intense feature of the total $2h$ spectra lies (see Fig. 1). We notice immediately the pronounced increase of the $C^{-1}F^{-1}$ component (red line) when the number of fluorine atoms increases from 1 to 3. For the heavier fluorobenzenes, while the $C^{-1}F^{-1}$ spectrum keeps increasing in intensity—and largely dominates the outer valence region—also the $F^{-1}F'^{-1}$ component (blue line) increases dramatically. This component shows a typical three-band pattern, similar to the...
F\textsuperscript{2} one but much more intense and characteristically shifted in energy. While all other components generally overlap over wide regions, the F\textsuperscript{-1}F\textsuperscript{-1} and F\textsuperscript{2} contributions never do and their regions of intensity exhibit a strict and characteristic alternation which we shall analyze later in detail. This will show that the evident demarcation at 54–56 eV of the

FIG. 3. (Color) Spectra of the 2\textit{h} population analysis decomposition for 1,2,3,4-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene. The one-site components are represented as shaded areas, the two-site as solid lines.
spectra (see Fig. 1) separates neatly the outer valence region from the inner valence, in that it corresponds essentially to the energy threshold at which ionization of the fluorine inner-valence ($2s$) electrons begins.

Overlapping regions in the population spectrum signal a corresponding delocalization of the double charge density among the components involved (of course, this is a strictly individual state property but, as many other features, it is widely shared among states underlying some evident structure in the spectra). Therefore, on the contrary, two holes created on the fluorine atoms are always strongly localized, either on a single atom or each on another atom. In sharp contrast with the two-site components involving fluorine, the $C^{-\text{I}}C^{-\text{I}}$ population is mostly confined and uniformly distributed over the outer valence region and it overlaps entirely the one-site $C^{-\text{I}}$ component. Like the latter, it has an essentially similar distribution for all molecules, both in shape and intensity, so that it is the largest component for benzene and mono-fluorobenzene. It is striking that the characteristically atomic three-band structure, which we have seen for the fluorine components, appears to be totally absent for the carbon ones. The typical $C^{-\text{I}}C^{-\text{I}}$ and $C^{-\text{I}}$ components clearly represent the pattern of charge delocalization over the aromatic ring and, except of details, stays surprisingly unaffected upon progressive substitution by fluorine atoms. In the next sections we shall be able to qualify these general observations more precisely.

V. ENERGY INTEGRATED TWO-HOLE POPULATIONS

Further insightful global information on the trends of charge distribution along the series can be obtained by studying in greater detail how the relative magnitude of the various population contributions changes with the number of fluorine substituents. The simplest picture is given in Fig. 4(A), where we have plotted the absolute total $2h$ populations summed over all states below 110 eV as a function of the number of fluorine atoms. For clarity, we have again omitted all the population terms involving hydrogen atoms, limiting ourselves to the five heavy-atom pairs which have the largest share of charge density. To frame the discussion, we mention that cutting the population integration at 110 eV corresponds to including 74%–75% of the total valence $2h$ space (excluding the hydrogen electrons) for all molecules except benzene, for which the proportion is a slightly larger 78%. The fraction of $2h$ space left out is determined not only by the states lying higher in energy than 110 eV, but also by the fact that we ignored individual states with a $2h$ weight less than 0.001. We call the curves of Fig. 4 energy integrated two-hole populations.

A number of interesting observations are immediately prompted by the data plotted. First of all, we underline that the data for all fluoro-benzenes studied are reported in the figure and where more than one isomer exists for a given number of fluorine substituents (2, 3 or 4), they are individu-
ally marked. It is remarkable then, as the figure shows, how very nearly coincident are the data points for different isomers, showing that the overall double-charge distribution depends with good accuracy only on the number of fluorine atoms and not their position (some deviations from this picture will be discussed shortly). We clearly see, further, that, as the number of fluorine atoms increases, the C\textsuperscript{-1}F\textsuperscript{-1} and F\textsuperscript{-1}F\textsuperscript{-1} populations grow fast and eventually dominate largely. In fact, the C\textsuperscript{-1}F\textsuperscript{-1} share is largest already in the di-fluorides, exceeding even the C\textsuperscript{-1}C\textsuperscript{-1} population. When the number of fluorine atoms is larger than three, also the F\textsuperscript{-1}F\textsuperscript{-1} population surpasses the C\textsuperscript{-1}C\textsuperscript{-1} one. The F\textsuperscript{-2} curve also increases from left to right and crosses the C\textsuperscript{-2} one at the di-fluorides.

Looking at the trends in the figure, one cannot fail to notice that the C\textsuperscript{-1}F\textsuperscript{-1} population appears to grow linearly with the number of fluorines, and so does the F\textsuperscript{-2} curve, although with a much smaller slope. By contrast, it is evident that the F\textsuperscript{-1}F\textsuperscript{-1} curve increases faster than linearly. Qualitatively, these trends are of course not surprising on the grounds of simple counting arguments, since the corresponding numbers of atom pairs have matching laws of growth: linear for the CF pairs (and F atoms) and quadratic for the FF\textsuperscript{2} pairs. But the curves appear to match these qualitative expected trends with remarkable precision, as is also confirmed by the eye-catching flatness of the C\textsuperscript{-1}C\textsuperscript{-1} and C\textsuperscript{-2} curves. This suggests to look at the populations per atom pair, which we have plotted in Fig. 4(B). This figure shows that the constancy of these values with the substitution level is, indeed, astonishingly precise. Significant deviations are observed only for the C\textsuperscript{-1}C\textsuperscript{-1} and C\textsuperscript{-2} curves, which decrease roughly linearly by about 20% and 28%, respectively, from benzene to hexafluorobenzene as an effect of the substitution. It is clear, indeed, that the C\textsuperscript{-1}C\textsuperscript{-1} and C\textsuperscript{-2} components should be most affected by the loss of hydrogen atoms: the latter share only a very small proportion of the two-hole density, thereby increasing that on the carbon atoms, while the opposite effect takes place with the electronegative fluorines. On the other hand, for the populations involving the fluorine atoms, the deviations from flat linearity of the curves do not exceed 5%. The main conclusions to be drawn from these findings are quite interesting. Except of the loss of hydrogen electrons, the two-hole density on the carbon ring stays remarkably constant over the fluorobenzene series. Furthermore, there is no significant cumulative effect of the fluorine atoms on the overall charge distribution across the double ionization spectrum: each added fluorine substituent plays the same role independent of the number (and position) of similar substituents already present.

Figure 4(B) shows that the share of two-hole density per atom pair varies widely from 2.5 (on average) for C\textsuperscript{-2} to about 20 for F\textsuperscript{-1}F\textsuperscript{-1}. These values are very interesting, as they can be used to estimate, albeit roughly and incompletely, the “effective” number of electrons available for double ionization on the corresponding atom pairs. There is a significant consistency among the data. For example, the average 2h population per pair of F\textsuperscript{-1}F\textsuperscript{-1} type is 19.7, implying that there are about 6.3 electrons available on each fluorine atom. (This is simply estimated by equating 19.7 to twice the square of the available orbitals, each doubly occupied.) From the average 5.7 2h pairs for C\textsuperscript{-1}C\textsuperscript{-1} we similarly calculate that about 3.4 electrons are available on each carbon. These numbers would imply about 10.6 2h pairs of C\textsuperscript{-1}F\textsuperscript{-1} type, a figure that matches exactly the corresponding average value of the data in Fig. 4(B). The estimated number of available electrons on carbon and fluorine appears to be somewhat small on account of the incompleteness of the spectrum. Their ratio (6.3:3.4) of 1.85 should be compared to the actual ratio of 1.75 between the valence electrons of fluorine and carbon. It is seen to be significantly larger, as a measure of the electron transfer from carbon to fluorine taking place in the ground state. We finally note that the average number of 2h pairs of one-site type (2.5 for C\textsuperscript{-2} and 8.3 for F\textsuperscript{-2}) are also roughly consistent with the other data, although they correspond to slightly smaller figures for the number of available electrons: 3.2 on C and 5.8 on F. (In the one-site case, the 2h population is equal to the square number of orbitals.) Especially for fluorine, this is not surprising, for a somewhat larger proportion of the one-site inner-valence density can be assumed to lie above 110 eV and is thus ignored in the present analysis.

Figure 4(B) also emphasizes some non-negligible spread of the data for isomers, which is most visible for the F\textsuperscript{-1}F\textsuperscript{-1} population of the di- and tri-fluorides. This is understandable in view of the fact that there is on average a much wider relative spread in F–F distance in these molecules than in the higher-substituted ones. For example, there is a large increase in the distance between the two F atoms on going from 1,2-difluorobenzene to the 1,3- and to the 1,4-isomers and this of course favors, other things being equal, F-F localization of the electron vacancies. Correspondingly, the F\textsuperscript{-1}F\textsuperscript{-1} population per pair increases from 18.69 for the ortho isomer to 19.36 for the meta, to 19.95 for the para. Similarly, the F\textsuperscript{-1}F\textsuperscript{-1} term for 1,2,4-trifluorobenzene is visibly larger than for its other two isomers because it is the only triply substituted species where localization of the holes on two fluorine atoms in the para position is possible. Another useful illustration of the global results for the two-hole density analysis may be given in terms of the fraction of total 2h population on each atom group, i.e., the absolute populations shown in Fig. 4(A) divided by the total. This is shown in Fig. 4(C) and evidences the fast decrease of the relative weight of the C\textsuperscript{-1}C\textsuperscript{-1} and C\textsuperscript{-2} terms in favor of the fluorine terms. Already for monofluorobenzene the C\textsuperscript{-1}C\textsuperscript{-1} population has shrunk to about half of the total and then again to about one third in the di-fluorides. Remarkably, in hexafluorobenzene the share of C\textsuperscript{-1}C\textsuperscript{-1} population has nearly decreased to the level of the one-site F\textsuperscript{-2} one. In relative terms, the C\textsuperscript{-1}F\textsuperscript{-1} contribution grows fast initially to become the largest already for the di-fluorides, but then flattens out and eventually starts decreasing. The F\textsuperscript{-1}F\textsuperscript{-1} population shows the fastest growth. The trends of the 2h fraction curves can be understood quite easily by recalling that the population per pair of a given type is approximately constant and that the total 2h population grows roughly as the total number of atom pairs. Therefore, the population fractions grow essentially as the corresponding fractions of atomic pairs. It is then clear why, for example, the F\textsuperscript{-1}F\textsuperscript{-1}
term increases linearly and why the $F^{-2}$ term is nearly constant (but increasing): since the total population grows quadratically with the number of fluorines, the $F^{-2}$ fraction is eventually destined to drop but in the physical number range of fluorine atoms, the quadratic term in the denominator is negligible and the fraction in fact increases slightly.

In consideration of the trends just discussed, we may even, in fact, normalize the charge fractions to the corresponding atom pair fractions, as is done in Fig. 4(D). This essentially shows the deviation of the charge distribution from the idealized situation in which each atom pair, regardless of the weight and nature of the component atoms, carries an equal share of the charge density (represented by an horizontal line at unity). As we can see the deviations are roughly within a factor of 2, exceeding it above for the $F^{-1}F'^{-1}$ component and below for the $C^{-2}$ component. The $C^{-1}C'^{-1}$ line drops below unity already in monofluorobenzene.

VI. ATOM PAIR POPULATIONS

A. $C^{-1}F^{-1}$ contributions

We would like now to study in greater detail how the various population components vary along the series. To gain some deeper understanding of the trends in the charge distribution it is clear that we need to examine the contributions of the several inequivalent atom pairs in a given broad group. The $C^{-1}F^{-1}$ component, which as we have seen is the dominating one over the whole series of fluorobenzenes, should be studied first and provides an interesting example.

As we discussed in relation to Fig. 4, the $C^{-1}F^{-1}$ population naturally grows substantially along the fluorobenzene series, but the average global number of hole pairs per CF pair is found to be remarkably constant, enclosed in the range 10.0–10.8. However, if we compare the energy distribution of the $C^{-1}F^{-1}$ component of the two-hole population, normalized to a single CF atom pair, we do see quite large changes in the series. This is best summarized by Fig. 5, which compares the unitary $C^{-1}F^{-1}$ components for the two end-points of the molecular series: $C_6H_5F$ and $C_6F_6$. Apart from a small shift at higher energy of the $C_6F_6$ spectrum, we notice that the shape and distribution changes substantially. In particular, there is a clear depletion of intensity at low energy, especially between 30 and 40 eV, which is roughly compensated by a corresponding enhancement at higher energies. The alteration of the $C^{-1}F^{-1}$ spectrum is smooth over the series of molecules, but is mainly visible only upon varying the number of fluorine atoms: the spectra of isomers are essentially identical.

To begin explaining these changes we need of course to look at the individual contributions of the various inequivalent carbon–fluorine pairs. The number of these pairs—and of their spectra—across the whole series of molecules is quite large but their study does reveal some evident patterns. In particular, essentially three facts appear to influence the two-hole population on a given CF pair: whether the carbon and fluorine atoms are directly bound, whether the carbon atom is bound to a different fluorine, and an additional larger increase of about 2 hole pairs on going from a fluorine-bound fluorine atom or to a hydrogen atom, and finally the distance between carbon and fluorine. In consideration of this, any given CF pair can be labeled as being of one of 7 types: $B$, $oF$, $mH$, or $pF$, when the carbon atom is hydrogen-bound and lies in ortho, meta, or para position to the fluorine-bound carbon, respectively; $oF$, $mF$, or $pF$, when the carbon atom is fluorine-bound and again lies in ortho, meta, or para position, respectively. This classification turns out, in fact, to be extremely accurate and helpful. We have computed the global population (i.e., the number of hole pairs over the whole double ionization spectrum below 110 eV), for all the CF pairs in the series of molecules (there are 234 of them) and the average results are as reported in the second column of Table I (total average 2$h$). It is evident that the population of each type is extremely well characterized, with nearly negligible variance, and it follows a precise pattern. There is a significant variation of about 1 hole pair depending on whether the carbon atom is directly bound to the fluorine or bound to a different fluorine, and an additional larger increase of about 2 hole pairs on going from a fluorine-bound fluorine atom or to a hydrogen atom.
TABLE I. Average number of hole pairs for each type of carbon–fluorine pair (classified as explained in the text) and relative abundance of CF pair types in the fluorobenzene series. The average population in column 2 refers to the whole double ionization spectrum below 110 eV, while that in column 3 to the outer-valence region only (the energy boundary of which varies slightly for each molecule).

<table>
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<th>CF pair type</th>
<th>Avg 2h</th>
<th>Pair type abundance</th>
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<td>o.v.</td>
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<td>$B$</td>
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</tbody>
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Carbon to a hydrogen-bound one. The distance between carbon and fluorine plays instead a relatively minor role, inducing variations of 0.2–0.4 hole pairs. (As expected, the population systematically increases with distance on account of a correspondingly smaller repulsion.) That the relative C$^-$F$^-1$ two-hole population should be smaller for CF pairs where the carbon atom is fluorine-bound, is also, of course, fully understandable in terms of the overall smaller electron density at such carbons in the ground state. Table I also shows the relative number of pairs of each type in the various molecules (normalized to 6) and, using these data, it is very easy to calculate an expected average number of hole pairs of C$^-$F$^-1$ type for the various molecules. Such estimates match practically exactly the data of Fig. 4(B).

As can be seen in the table, each molecule in the series is characterized by a unique distribution of CF pair type abundance. However, it is important to notice that the relative number of pairs in each of the broader classes, that is to say, directly bound pairs ($B$), pairs with a fluorine-bound C atom ($xF$) and pairs with a hydrogen-bound carbon ($xH$), is constant among isomers. Relative to each $B$-type pair, the number of $xF$-type pairs goes from zero to 5 on going from $C_6H_5F$ to $C_6F_6$, increasing by one for each added fluorine atom. The number of $xH$-type pairs follows of course the exactly opposite trend. Since the relative weight of the broader classes is what essentially only affects the average C$^-$F$^-1$ population, with only marginal additional effects of the CF distance, this helps explaining the close similarity of the C$^-$F$^-1$ spectra of isomers.

The above discussion now gives us a simple and firm framework in which to study the observed changes in the global C$^-$F$^-1$ population (Fig. 5): we essentially only need to examine the variation of the 7 C$^-$F$^-1$ subtypes with energy. This analysis shows that the differences in the average 2h population that we have just discussed are in fact entirely occurring in the outer valence region and are even exceeded there. This is easily explained since it is the outer-valence carbon electrons which are mostly drained upon binding fluorine, decreasing their availability for ionization. The results are shown in the third column of Table I (the variances are always less than 0.07). As we have seen by looking at the spectra, the energy boundary of the outer-valence region changes somewhat for each molecule (between 53.6 and 55.9 eV), and has been carefully identified in each case by close examination of the spectra. As a consequence of the trend in the outer valence, the mean population changes in the opposite direction in the inner valence for compensation: it it slightly larger for $B$-type and $xF$-type pairs (average 2.4) than for $xH$-type pairs (average 2.2). These findings account quite satisfactorily for the mechanism through which the C$^-$F$^-1$ spectra change along the fluorobenzene series, as we have observed in Fig. 5.

B. Carbon double hole contributions

The study of the C$^-$C$^-1$ and C$^-2$ components of the two-hole population is of particular interest because they essentially represent the portion of double-charge density carried by the benzene ring. The variation of these components along the fluorobenzene series, therefore, shows a fundamentally important aspect of the change in the electronic structure induced by fluorine substitution and probed by double ionization.

As reference frame for the discussion we should start by illustrating the situation in the benzene molecule itself, which is summarized in Fig. 6. The total C$^-$C$^-1$ component of the population here dominates strongly and is distributed fairly uniformly over the energy region below about 50 eV. It does, however, show a significant fluctuation of intensity, which results (in our convolution shown as a red line in the top panel of the figure) in a number of distinct peaks of comparable strength. It is not difficult to see that the ultimate origin of these features is to be found in the underlying clustering of electron-pair energies, which is in turn determined by the orbital and hole repulsion energies. This is shown quite clearly by the convolution of first-order double ionization energies plotted as a black line (of arbitrary uniform intensity) below the C$^-$C$^-1$ line in the top panel of the figure. The first-order spectrum has been shifted down by 5.7 eV in order to align the double-ionization threshold. It is evident that the C$^-$C$^-1$ spectrum bears clear traces of the first-order structure, although it is strongly altered by correlation effects.

The fact that a roughly similar overall distribution is found for the C$^-$C$^-1$ component of the two-hole population and for the one-particle Hartree–Fock double ionization energies already suggests the answer to a fundamental question: the double-charge density in the benzene dication is...
largely delocalized over the whole ring. This is not particularly surprising but it is not obvious \textit{a priori} either. Hole repulsion produces a drive towards charge separation and, since the distance between carbon atoms of different CC pairs varies appreciably, this may induce localization of the holes on atom pairs in para position at low ionization energy, and a corresponding localization on closer-lying atom pairs at progressively higher energies. This is in fact what typically happens in simple ionic or weakly bound systems.

Screening of the electron vacancies through delocalization over the aromatic ring contrasts this tendency and the fact that such delocalization prevails is confirmed by the two-population analysis: essentially all states have comparable 2\(h\) population on any \(C^{-1}C'^{-1}\) pair, regardless of C–C distance, although the one-site \(C^2\) population is generally much smaller. The bottom panel of Fig. 6 shows this by displaying the decomposition of the carbon double hole density into its partial inequivalent contributions. The figure

FIG. 6. (Color) (Top) Total \(C^{-1}C'^{-1}\) 2\(h\) population for \(C_6H_6\) and distribution of the first order double ionization energies. (Bottom) One-site \(C^2\) 2\(h\) population for \(C_6H_6\) and decomposition of the \(C^{-1}C'^{-1}\) population into ortho-, meta-, and para-contributions.
shows clearly that all the components share a very similar distribution. Among the two-site contributions, the ortho component is, to be sure, slightly less intense in general, especially at low ionization energies, but it shows a peculiar peak at about 45 eV which is not present in the meta and para components. The latter components, on the other hand, exhibit an extremely similar spectrum. A concise summary of the differences is provided by the integrated two-hole population figures, which yield 6.1 hole pairs per ortho CC pair, 6.5 per meta pair and 6.6 per para pair. (Of course, in the global distribution, one must then take into account the fact that there are only half as many para CC pairs as meta or ortho ones.) The one-site population is seen to have a similar distribution and peak structure, especially similar to the ortho two-site one, but it is uniformly much weaker: its integrated value (per carbon atom) is roughly half as large (2.9).

Having discussed the main features of the two-hole density in the benzene dication, we should now examine how this is altered when hydrogen is substituted by halogen atoms. The amount of detailed data computed is vast, permitting an accurate description of these changes as a function of the substitution level in various regions of the ring or for the various groups of inequivalent carbon pairs (there are, in all, over 100 of them). We must therefore be selective, giving some examples and enunciating the main results. All our data are of course available to interested readers.

It is best to start by examining the case of monofluorobenzene, which one can expect to show the essential nature of the effects of substitution. Figure 7 (top) compares the total C−1C−1 distribution between 25 and 35 eV. The amount of detailed data computed is vast, permitting an accurate description of these changes as a function of the substitution level in various regions of the ring or for the various groups of inequivalent carbon pairs (there are, in all, over 100 of them). We must therefore be selective, giving some examples and enunciating the main results. All our data are of course available to interested readers.

One interesting question is that of the spatial extent of the effects of fluorine substitution. We expect of course the five components of the C−1C−1 population involving the fluorine-bound carbon to be mostly affected, but we would like to establish what is the response of distant regions of the aromatic ring. The middle and bottom panels of Fig. 7 show some of the C−1C−1 components in benzene and monofluorobenzene which illustrate this point. In the middle panel, the unitary para C−1C−1 distribution of benzene is compared with the C−1C−1 component of fluorobenzene. As expected, we see that the differences are quite large and, most important, extend here over the whole outer valence energy region. The integrated population shows that the global decrease for this pair is from 6.6 in benzene to 5.6 in monofluorobenzene. The ortho and meta components involving the substitution site shows similar patterns of alteration. The global population decreases for the ortho component is from 6.1 to 5.1 and for the meta component is from 6.5 to 5.3. The bottom panel of the figure shows instead the comparison of the ortho C−1C−1 component of benzene with the C−1C−1 component of fluorobenzene, i.e., the corresponding ortho component farthest away from the substitution site. As can be seen, even here surprisingly significant alterations of the charge distribution are still visible, especially at low energy, although the integrated intensity is hardly affected (it decreases...
from 6.1 to 6.0). The other components of the $C^{-1}C^{-1}$ population also show remarkable spectral changes of qualitatively similar appearance. The integrated populations follow an even more complicated pattern: while those of pairs far away from the substitution site tend to decrease slightly (as we have just said of the ortho component), the double charge density on CC pairs involving hydrogen-bound carbon atoms closer to the substitution site show a general tendency to increase slightly. This is very well exemplified by the results for the meta component (which is 6.5 in benzene): in monofluorobenzene there are three inequivalent such components not involving $C_1$ and, while the one farthest away from $C_1$, namely, $C_3^{-1}C_1^{-1}$, has a global population of 6.3, the $C_2^{-1}C_4^{-1}$ figure is 6.8, and it is 6.9 for the closest lying $C_2^{-1}C_6^{-1}$ pair. This tendency is observed also in higher substituted fluorobenzens. We may interpret all these data as showing that the aromatic ring polarization induced by the presence of fluorine has quite far reaching and complicated effects. By draining electron density towards the substitution site, it slightly impoverishes distant carbon atoms but enriches more appreciably closer lying carbons. In general, our results demonstrate with great detail how the resilience of the aromatic ring, shown for example by the global $C^{-1}C^{-1}$ distribution of Fig. 7 (top), is the result of a complex and long-range propagation of electronic effects. Double ionization, by revealing correlated electron pair properties, is an extremely sensitive probe of chemical differences.

We should finally comment on the essential changes in the one-site $C^{-1}$ ring population induced by fluorine substitution. Such changes are of fundamental importance to understand, for example, the carbon KLL Auger spectra of these molecules, which we shall briefly discuss later. The calculations show that the $C^{-1}$ components follow an essentially similar trend to that of the two-site components. There is a global alteration of the distribution which is quantitatively localized in the lowest energy region but is qualitatively pronounced, even more clearly than for the two-site population, also at higher energies. At the first hydrogen → fluorine substitution, the global decrease in population from 17.4 to 16.3 hole pairs is almost entirely taking place at the substitution site (from 2.9 to 2.0), but there is a significant alteration of the spectral shape of the $C^{-1}$ population even at the carbon site in the para position, although its integrated population stays unchanged. Confirming fully the picture emerged from the analysis of the two-site components, we find that the total one-site population on the carbon in the meta position decreases slightly (2.7), while that on the neighboring ortho carbon tends to increase (3.0).

Having examined the main effects of replacing one hydrogen atom with one fluorine on the benzene ring, we should now briefly illustrate the changes occurring as the number of fluorine substituents is increased. What we essentially observe here is that the two-hole density on the carbon ring is altered in ever more significant details, and its distribution is also shifted at higher double ionization energy. The basic changes we have seen upon introducing the first fluorine atom serve quite well as a guideline to explain the effects of further substitutions. We recall that, as previously observed, there is hardly any synergic effect in the fluorine progression. In fact, as Figs. 2–4 are enough to illustrate, the main characteristics of the $C^{-1}C^{-1}$ and $C^{-2}$ distributions remain remarkably stable and recognizable throughout the series, even beyond what may be expected after the analysis of $C_6H_4F$. There is one specific mechanism which helps maintain such stability that we would like to describe. If one looks at the substitution sites of the ring, there are no surprises: the electron depletion at the fluorine-bound carbon atoms follows a pattern which is predictable from the previous analysis. Thus we see that the average integrated $C^{-1}C^{-1}$ population for CC pairs with one fluorine-bound and one hydrogen-bound carbon atom varies from 5.4 for ortho pairs to 5.9 for para pairs, with variances well below 0.1 throughout the whole series. These averages are slightly higher than the values for monofluorobenzene previously mentioned, as might be expected. The global two-site populations for CC pairs where both carbons are F-bound decrease roughly by a further unit to 4.6 for ortho pairs, 4.7 for meta pairs, and 4.9 for para pairs. This is again in full accord with the lack of cooperative effects in multiple substitutions. The electron depletion at the substitution sites, however, is contrasted by a smooth but marked tendency to increase the two-hole population at those carbon pairs which remain (up to the tetrafluorobenzens) hydrogen-bound. We thus see, for example, that the ortho $C_3^{-1}C_6^{-1}$ population in 1,2,3,4-tetrafluorobenzene (i.e., the sole two-site term remaining where both carbons are H-bound) is computed to be 6.7. Similarly, the meta $C_4^{-1}C_6^{-1}$ population in 1,2,3,5-tetrafluorobenzene is 7.4 (nearly one unit higher than benzene) and the para $C_3^{-1}C_6^{-1}$ term in 1,2,4,5-tetrafluorobenzene is 7.3.

The modification of the one-site $C^{-1}$ spectral distribution along the fluorobenzene series is summarized in Fig. 8 where, to avoid cluttering the figure, we just compare the spectra for benzene, 1,2,3-C$_6$H$_3$F, and hexafluorobenzene. As can be seen, the relative changes are both qualitatively and quantitatively large. At low energy there is an almost complete quenching, by about 73% over the series, of the strength of the first three peaks. At higher energies, the overall drop in intensity is not so dramatic although the spectral profile is still altered substantially. Interestingly, there is an energy window, between 35 and 40 eV, where the $C^{-2}$ population remains almost unaffected by fluorine substitution. We computed that the decrease in total $C^{-2}$ population below 34 eV is from 4.8 in $C_6H_6$ to 1.3 in $C_6F_6$, but it is only from 3.4 to 2.3 between 35 and 40 eV. As may be expected by now, the changes in the spectra, even more accurately than for the less space-localized components of the 2h density, must be ascribed practically entirely to the fluorine-bound carbons: the $C^{-2}$ spectra of hydrogen-bound C atoms remain much more similar throughout the series, and their integrated population is also approximately constant or even slightly increasing with the number of fluorine substituents.

### C. Fluorine double hole contributions

As Figs. 2 and 3 show, the energy distribution of the pure-fluorine components of the 2h density, $F^{-1}F^{-1}$ and $F^{-2}$, could hardly be more strikingly different from the car-
bon ones. Whereas the latter show a broad distribution, quite uniform over the whole spectrum although more intense in the low-energy half, the fluorine components appear as narrower and well separated bands, very evident up to about 100 eV, with practically no intensity in between. Furthermore, as we have already pointed out, bands of F$_{2}$$_{1}$F$_{8}$$_{2}$ type alternate with bands of F$_{2}$$_{1}$ type and their overlap is very small.

The pattern of the fluorine two-hole density components is in fact very simple to understand: it is quite similar to the double ionization spectrum of first-row isolated atoms. We can comfortably explain it in terms of fluorine atomic orbitals and even the energy separation of the bands can roughly be related to the energy spacing between the 2s and 2p orbitals of fluorine ($\approx$ 24 eV, for atomic fluorine). Let us inspect first the spectra of the one-site F$_{2}$$_{1}$ component, where four well defined, structured bands are to be seen (full green areas in Figs. 2 and 3). The whole spectrum shifts quite rigidly to higher energy by about 0.6 eV for each added fluorine atom, except for C$_{6}$F$_{6}$ where the shift with respect to pentafluorobenzene is about 0.9 eV. The first band at low energy peaks at about 46 eV in C$_{6}$H$_{5}$F. This band is the most intense and corresponds essentially to the double ionization of 2p electrons on a single fluorine atom. Between 65 and 80 eV we then see two other intense and very nearly equal features. These bands arise from the ionization of one 2p and one 2s electron of a fluorine substituent. Because of the compact 2s electron density, there is a large energy split (of the order of 10 eV) between triplet and singlet coupling of the holes. The lower energy band corresponds to triplet coupling and the higher energy one to singlet coupling. Finally, in the region between 96 and 100 eV there is one relatively weaker band related to double ionization of a single fluorine 2s electrons. It is interesting to note that, in accord with this assignment, practically no singlet state contributes to the F$_{2}$$_{2}$ spectra above \( \sim 93 \) eV.

The three strong and broader bands of the F$_{2}$$_{1}$F$_{8}$$_{2}$ component are also easily explained: the lowest energy one, especially intense between 30 and 40 eV, is also due to the ionization of two outer-valence (2p) fluorine electrons, the middle one, around 60 eV, to the loss of one outer-valence and one inner-valence electron, and the high-energy band just above 80 eV to ionization of two inner-valence electrons. The only difference is that here the two electrons come from two different fluorine atoms. As a consequence, because of the smaller repulsion between the holes created, the bands lie at lower energy than the corresponding one-site ones. Also, there is no large singlet–triplet splitting of holes localized on distant atomic sites and so we see a single band in the middle of the spectrum instead of the two one-site ones. The one-site and the two-site bands are relatively narrow and do not overlap because of the obvious energy difference between the different and clear-cut hole localization patterns.

The fluorine two-hole populations show therefore that the fluorine substituents, in sharp contrast with the carbon atoms, essentially retain their atomic electronic structure. This is qualitatively not surprising. The carbon atoms are involved in the formation of multiple covalent bonds in the aromatic system and, furthermore, become strongly electron-deficient upon binding fluorine. In such chemical environment their atomic nature is thoroughly lost. By contrast, the fluorine substituents are strongly electronegative and are involved in the formation of a single polarized chemical bond with the aromatic ring. The presence of this strong bond is
reflected mainly in the broad and intense $\text{C}^{-1}\text{F}^{-1}$ component of the two-hole density, which mostly borrows intensity from the benzene ring. The $\text{F}^{-1}\text{F}^{-1}$ and $\text{F}^{-2}$ contributions, therefore, reflect the ionization of the remaining, largely unaffected, fluorine atomic cores.

Conclusive evidence of the inherent atomic nature of the fluorine two-hole density spectra is the fact that the $\text{F}^{-2}$ distributions of all molecules (once the electrostatic energy shifts and the intensity factors due to fluorine abundance have been taken into account) are almost quantitatively indistinguishable, entirely unaffected by the chemical environment. In fact, their extreme invariance is reminiscent of—if not even more pronounced than—core ionization spectra. The contrast with the large variability of the $\text{C}^{-2}$ spectra discussed earlier (see Fig. 8) is, once again, striking. The $\text{F}^{-1}\text{F}^{-1}$ components are also very similar, except of energy shifts, across the whole fluorobenzene series, although there are somewhat more perceptible differences. Interestingly, for the $\text{F}^{-1}\text{F}^{-1}$ population the differences among molecules with different number of fluorine atoms are qualitatively comparable to differences among isomers: the difference in distance between fluorine atoms obviously plays here its most important role. It should be mentioned that some effects due to different distances between similarly placed fluorine pairs exist also between fluorobenzenes with different substitution levels.

VII. ON THE EXPERIMENTAL DOUBLE IONIZATION SPECTRA

The study of the double ionization of fluorobenzenes, and especially the detailed description of the two-hole density in the dicaticonic states afforded by the population analysis, allows us to make an informed discussion of their experimentally measurable spectra. Let us start with the carbon and fluorine $\text{KLL}$ Auger spectra. The main notion on which we base our discussion is that the Auger decay following the ionization of a deep core electron is predominantly an intraatomic process, in the sense that the final states are populated with a probability which is in qualitative relation to their hole-localization at the atomic site of the initial, strongly localized, core vacancy. This can be justified by a simple approximation of the Auger transition rates (see, e.g., Refs. 19–21) and was proposed originally in Ref. 22. On these grounds, we may simply estimate the Auger spectra by looking at the one-site components of the $2h$ population, since these give an unambiguous measure of precisely the extent to which the two final holes localize on a given atom. This approach has in fact been satisfactorily used in a number of previous theoretical studies on Auger spectra (see, e.g., Ref. 23, and references therein). The approximation works well on average, especially when the density of final dicaticonic states is high enough that the bands in the spectrum are shaped by the contribution of a very large number of transitions. This is the normal situation save for very small molecules and the low energy end of the ionization spectrum.

Except for details, therefore, the appearance of the Auger spectra of the fluorobenzenes is as may be inferred by the discussion in the preceding section, and can be summarized as follows. For any of the fluorobenzenes, the Auger spectra following ionization of the carbon 1s and fluorine 1s shells look totally different, because they probe totally different characters of the doubly ionized states. The fluorine spectrum is essentially a relatively simple atomiclike spectrum, where only four distinct, well separated, bands dominate. In order of increasing speed of the outgoing Auger electron, these bands correlate strictly, as we have seen, to atomic $2s^{-2}$, $2p^{-2}12s^{-1}$ (triplet and singlet), and $2p^{-2}$ states, respectively, the latter being most intense. In the $2h$ population analysis we have seen that two equally dense groups of states of $2p^{-1}12s^{-1}$ type can be identified, differing for the spin coupling of the holes. However, on the basis of a simple independent-particle analysis of the Auger intensity we should expect the triplet states to have a much smaller rate. Because of the characteristic energy distribution of the $\text{F}^{-2}$ hole density in the dicaticonic states, which is large in the groups of states just mentioned and almost vanishing everywhere else, therefore, the fluorine spectra are highly selective. The F 1s Auger spectrum measured for hexafluorobenzene conforms exactly to this interpretation.

By contrast, the carbon Auger spectra have a very complex structure with many broad and overlapping peaks, where a huge number of dicaticonic states contribute. The spectra should have significant intensity only up to about 65 eV (DIE), but while in the fluorine case they have nearly vanishing intensity for all the dicaticonic states below 46–50 eV, the carbon spectra start at the DIE threshold (about 20 eV lower!). They are essentially unselective spectra, in the sense that they manifest the whole manifold of doubly ionized states, and their overall appearance is expected to be qualitatively not unlike that of the Auger spectrum of benzene. As we have seen, this complexity arises from the essential fact that, due to the strong aromatic bonding, all traces of the simple atomic electronic structure of carbon are lost and the $\text{C}^{-2}$ two-hole density is distributed over the whole outer-valence double ionization spectrum. Again, the only measured C 1s spectrum, that of $\text{C}_6\text{F}_6$, represents indeed a perfect example of this character.

What is more important, there is a great difference between the fluorine and carbon Auger spectra in their sensitivity to the chemical environment. As we have explained of the $\text{F}^{-2}$ population, its distribution is nearly identical for all molecules in the series (and in fact, expectedly very similar in most fluorides), except of a shift of about 0.6–0.9 eV to higher double ionization energy for each added fluorine atom. A pronounced invariance, except of the chemical shift, should therefore characterize also the Auger spectra. On the contrary, we have seen that the $\text{C}^{-2}$ distribution changes very significantly along the fluorobenzene series, especially because of a massive loss of intensity at low double ionization energy which results from binding fluorine. As a consequence, we should expect that the carbon Auger spectra for different molecules are sufficiently different to serve as a clear tool of identification. Fluorine and carbon core ionization give rise, in conclusion, to two totally different flavors of Auger spectra. The former one is the quintessential atomiclike spectrum whose properties are widely exploited as a tool of analysis for atom detection in materials. The other is...
a typical molecular Auger spectrum, where chemical bonding disrupts the electronic structure of the atom to the extreme, making the spectrum, at the same time, sensitively responsive to the chemical surroundings. The character of the latter kind of Auger spectra was first discussed for some small fluorides\textsuperscript{11,23,24} and aptly named \textit{foreign imaging}. The present results represent an extension of this model. In small fluorides, where a central atom is saturated with halogen ligands, electron depletion at the central site and hole localization at the ligands—either of one-site or two-site type—shape almost entirely the foreign-imaging spectrum. The latter appears, to a large extent, as the superposition of the typical F\textsuperscript{2−} and F\textsuperscript{−}F\textsuperscript{−} spectra.\textsuperscript{24} In the present case, the aromatic ring electronic structure gives a characteristic global band shape to the carbon spectra, and the presence and number of fluorine substituents provide a complex fingerprinting superstructure.

As a relevant side aspect of the wide variability of the carbon spectrum, it should also be considered that inequivalent carbon atoms in any of the fluorobenzenes have in principle slightly different core ionization energies. In fact, presumably, the C\textsubscript{1}s binding energies of, say, a hydrogen-bound and a fluorine-bound carbon atoms might be different enough (of the order of 2.5 eV at the Hartree–Fock level) to open the possibility of selectively core-ionizing one or the other. The ensuing Auger decay would then, in practice, be probing different components of the C\textsuperscript{2−} density, localized at corresponding different sites of the benzene ring. Such measurements would be a quite interesting workbench for the two-hole density analysis.

Finally we would like to make some comments, in so far as our calculations allow us, on the double charge transfer (DCT) spectra of the fluorobenzenes. These have been measured for a number of them,\textsuperscript{3,7–9} as well as for benzene,\textsuperscript{6} employing different projectile cations and resolutions. The use of different projectiles is particularly useful for mainly two reasons. First of all, in so far as the charge stripping collisions are spin-conserving and the initial and final spins of the projectile (before and after it has undergone double electron capture) are fixed and known, different cations may be used to selectively populate triplet or singlet dicaticonic states of the target. For example, OH\textsuperscript{+} or F\textsuperscript{+} projectiles in their triplet ground state populate triplet dicaticonic states of the target if they end up as singlet anions, OH\textsuperscript{−} and F\textsuperscript{−}, after the collision. Similarly, H\textsuperscript{+} projectiles are typically used to measure singlet double ionization energies. Second, the energy window of useful cross section for the charge stripping is relatively narrow, and so projectiles with different double electron capture affinity may be used to move the energy window of doubly ionized states investigated.

Separating singlet from triplet states does bring some degree of simplification but, because of the charge-stripping collision problem, computing the intensity distribution of DCT spectra is not any easier than for the Auger process, even at the level of rough estimates. Based on perturbation theory, one may just assume that the target dicaticonic states are preferentially populated, as a rule, when their straight 2h character is large. DCT spectra typically display a jagged profile, made up of many narrow and closely spaced peaks, whose details seem to depend very sensitively on the projectile and its speed. This fact, combined with the high density of states in the double ionization spectra, makes it rather awkward and unreliable, in our experience, to attempt an analysis of the DCT peaks based on the comparison of observed and computed DIE values, except perhaps at the threshold.

To give an example of the difficulties we have just mentioned, we report in Fig. 9 the computed 2h bar double ionization spectra of hexafluorobenzene, together with the experimental DCT DIEs.\textsuperscript{9} The upper panel shows the singlet states and the lower panel the triplets. Each bar has a height proportional to the computed 2h weight (whereby degenerate states are typically higher) and the DCT peak positions are shown as dots. The computed spectra have been shifted in energy in an attempt to obtain a reasonable alignment with the experimentally reported lowest peaks. In the singlet spectrum, it would seem that the first three experimental dots may be interpreted by the calculations, as they match quite well the first three group of states. At higher energies, things rapidly get much more complicated: the DIE peaks extracted from the measurements do not seem to match the computed spectrum in any discernible pattern, nor do they reflect the sudden increase in density of states. The triplet spectrum shows very similar—worse if possible—problems. Two closely spaced peaks at the threshold have been reported from the experiments,\textsuperscript{9} where only one state is computed. Similarly, there do not seem to be triplets (of appreciable 2h weight) between 29 and 30 eV where again two DCT peaks are reported. In general the density of experimental peaks is higher than in the singlet spectrum, not so the theoretical density of states. One might surmise that the experiment using OH\textsuperscript{+} projectiles was not strictly spin-selective. Concerning the threshold discrepancy, it should be mentioned that in a previous (lower resolution) experiment, only one triplet DCT peak was found instead of two.\textsuperscript{3} On the other hand, in the same work, first order propagator calculations (thus in principle of lower accuracy than ours) were reported to give two triplet states, not one, which turn out to match closely the newer experiment. These discrepancies between our calculations and previous work might be easily settled by performing yet more accurate \textit{ab initio} calculations on the lowest-lying dicaticonic states of hexafluorobenzene. But in all evidence, much more work, both theoretical and experimental, must be done before the information contained in DCT spectra can be usefully unraveled.

\textbf{VIII. SUMMARY AND CONCLUSIONS}

In the present work we have presented a detailed analysis, based on correlated \textit{ab initio} Green’s function calculations, of the charge density distribution in the doubly ionized states of the series of fluorobenzene molecules, as well as of benzene itself. The double ionization spectra are extremely dense and many tens of thousands of states have been computed. A consistent interpretation of the results has been made possible by a population analysis scheme to partition the 2h spectroscopic factors of the Green’s function in atomic-pair components. This permits a quantitative spatial mapping of the two-hole density which unveils several and
detailed aspects of the electronic structure of the molecules, as is probed by double ionization. In particular, a detailed study was made of the effects of the progressive hydrogen substitution by the halogen atom along the series and of the changes in the hole density as function of energy. This can be described in terms of hole localization/delocalization patterns and of the competition between the aromaticity of the benzene ring and the disruptive electronegativity of fluorine. The aromatic electronic structure is shown to be extremely resilient and at the same time detectably responsive to hydrogen substitution. As a consequence, to a surprisingly large extent, successive fluorine additions do not exhibit any synergy. The double ionization process is an extremely sensitive tool of electronic structure analysis. The $2h$ population analysis provides a very useful key for the interpretation of the Auger spectra of the fluorobenzenes in terms of the foreign-imaging/self-imaging model. The F 1$s KLL$ Auger spectra are strictly invariant atomiclike spectra throughout the series, while every trace of the free atom is lost in the C 1$s$ spectra. These exhibit a typical aromatic ring appearance throughout the fluorobenzene series and, especially in the low DIE region, show fingerprinting features of the chemical environment. The double charge transfer spectra are also briefly discussed, showing that, except at the double ionization threshold, their interpretation is more difficult than previously thought.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge financial support by C.N.R. and thank L. S. Cederbaum for helpful comments on the manuscript.

8. GAMESS-UK is a package of *ab initio* programs written by M.F. Guest, J.H. van Lenthe, J. Kendrick, K. Schoffel, and P. Sherwood, with contributions from R.D. Amos, R.J. Buenker, H.J.J. van Dam *et al.* The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS), 1980.