

Foreign Imaging in Auger Spectroscopy: The Si 2p Spectrum of Silicon Tetrafluoride

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We performed Green's function calculations on the double ionization of SiF₄ in order to interpret its Si 2p Auger spectrum, which has caused controversy for a decade. We provide an accurate interpretation and a model of far wider generality in the Auger study of ionic species. Contrary to the usual *self-imaging* picture of Auger spectroscopy, the silicon spectrum exhibits eight distinct bands reflecting a complete and precise image of the fluorine ligands, due to strong hole-localization effects. The generality of this *foreign-imaging* character of Auger spectroscopy is discussed.

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Auger spectra of molecules and solids are usually thought of as fingerprinting images of the atoms where the primary inner shell electron vacancy is created, because the strong atomic localization of the core hole is such that the Auger decay rate matrix elements are dominated by intra-atomic terms. In turn, this picture has generally led to the expectation that molecular Auger bands broadly reflect double electron vacancies in the *atomic* valence shells and the chemical bonding environment producing a modulation, however significant, over this underlying atomic structure. Thus one can often identify, for example, three distinct band regions in the spectra of molecules containing first and second row atoms, which correspond to doubly ionized states where the two holes involve either the outer-valence or the inner-valence shell, or both shells, of the atom whose spectrum is being measured. Obvious prototype examples for such interpretation are first and second row hydrides: The central atom Auger profiles invariably present a well separated three-region structure due to double-hole states that strictly correlate with atomic p^{-2} , $p^{-1}s^{-1}$, and s^{-2} valence holes, respectively.

That this atomic *self-imaging* picture of molecular Auger spectra may apparently fail to meet even qualitative success is, however, indicated already by a number of experimental spectra of simple molecules, and notably of some strongly ionic first and second row halides [1,2]. A clear-cut example is represented by the silicon $L_{2,3}VV$ Auger spectrum of gaseous SiF₄, which has been the subject of several studies and diverse, conflicting interpretations, over a time span of almost a decade [1,3-6]. Instead of the three-band regions which would be expected on the basis of the self-imaging model (and which are found, e.g., in the Si spectrum of silane [7]), the experimental spectrum, reproduced in Fig. 1(c), shows six broad bands, roughly equally spaced. Some qualitative interpretations have been put forward to account for this unexpected profile [1,3,4]. Very recently there have been attempts [5,6], accompanied also by molecular orbital

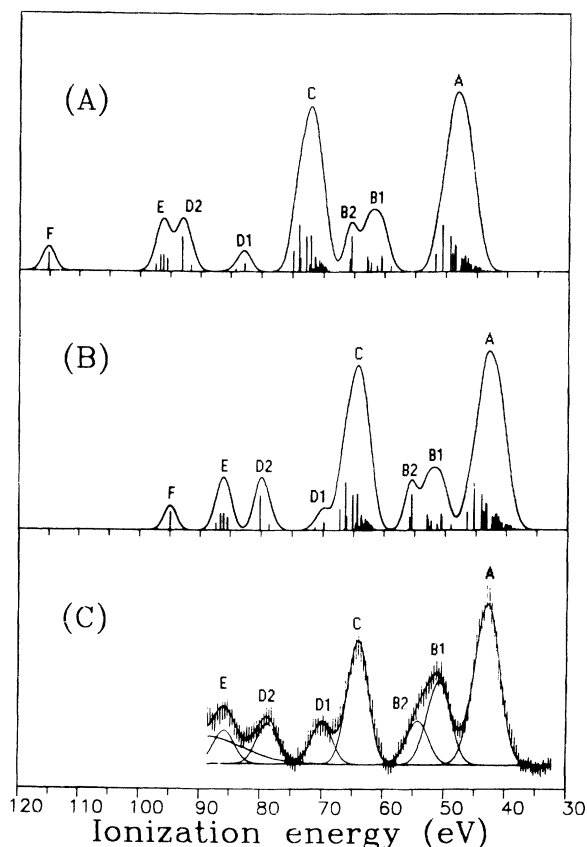


FIG. 1. (a) Theoretical Si 2p Auger spectrum of SiF₄ obtained by Gaussian convolution (FWHM 2.5 eV) of the Si⁻² two-hole populations (shown as a bar spectrum) resulting from the ADC(2/2*h*) calculations. The peaks are labeled as the corresponding groups of states in the table. The spectrum is not corrected for relaxation energy shifts. (b) Theoretical Si 2p Auger spectrum of SiF₄ obtained as in (a) and corrected for relaxation energy shifts (see text). (c) Experimental Si 2p Auger spectrum of SiF₄ reproduced from Ref. [3] and reported on the double ionization energy scale.

calculations [6], to reconcile the experimental findings with the self-imaging picture, by attributing three “extra” features to secondary (shake up and shake off) processes accompanying the primary ionization and the Auger decay.

The accurate calculation by *ab initio* methods, including electron correlation, of the thousands of dicationic states contributing to the Auger spectra of a penta-atomic species has so far appeared to be a prohibitive obstacle to the quantitative and conclusive interpretation of the spectra of SiF₄. We show in this Letter that, due to the inherent simplicity of the strongly ionic bonding in SiF₄, a complete and even quantitative understanding of its Auger spectra can in fact be achieved without the accurate calculation of *all* the states in the double ionization spectrum. We have performed, using a triple-zeta basis set including polarization functions, extensive Green’s function ADC(2) (algebraic diagrammatic construction scheme in second-order perturbation theory) [8,9] calculations on the lowest several hundreds of double ionization transitions, which lie in the energy range of the first two bands in the silicon spectrum and the first one in the fluorine spectrum. These calculations, which involve an eigenvalue problem over the whole set of two-hole (*2h*) and three-hole-one-particle (*3h1p*) configurations built from the Hartree-Fock neutral ground state orbitals, provide the double ionization energies and spectroscopic factors of the main (diagram) and satellite dicationic states. All the details of these calculations will be given elsewhere [10]. Using these accurate results it is possible to suitably scale the results of less accurate calculations extending over the *whole* double ionization spectrum. This has allowed us to accurately reproduce all the features of the Si spectrum of SiF₄ and conclusively interpret them. Our results reveal in fact a completely general and consistent picture of the Auger spectroscopy of strongly ionic systems.

To obtain the above mentioned approximate but consistent picture of the Auger spectra of SiF₄ over the whole valence double ionization spectrum, we have carried out restricted ADC(2) calculations including only the *2h* configuration space [ADC(2/*2h*)]. Such calculations already account for the “internal” *2h/2h* part of final state correlation. In particular this restricted scheme is already sufficient to describe to a very large extent the final state hole-localization effects which, on the basis of previous experience [11], are expected to be of crucial importance for the description of double ionization in strongly ionic systems. It is worth recalling here that double-hole localization on equivalent atoms cannot be described at all in a consistent way within the framework of variational independent particle (molecular orbital) methods [11]. The main shortcoming of the ADC(2/*2h*) calculation is its inability to fully describe final state relaxation effects, which are expected to be very relevant. However, as will be discussed, final state

relaxation can consistently be estimated with remarkable accuracy, thus largely overcoming this deficiency. The “external” electron correlation introduced in the ADC calculations through *3h1p* excitations is also, of course, neglected in ADC(2/*2h*). In general, for strongly covalent and multiply bonded systems where the appearance of strong satellite lines can constitute an important phenomenon, this would represent a very severe limitation. But previous experience [11] indicates that this causes only minor effects on the Auger band shapes of strongly ionic systems.

The *2h*-space valence shell double ionization spectrum of SiF₄ comprises 107 dicationic states (with *T_d* symmetry labels). To easily interpret the electronic structure of these states we have carried out a two-hole atomic population analysis [11] of the ADC eigenvectors. This allows us to analyze the spatial distribution of the two electron vacancies over the molecular region, and in particular to obtain a quantitative measure of hole-localization effects. The results offer an unambiguous and illuminating picture which is not subject to modification, except of quantitative details, in the more accurate full ADC(2) calculations. *All* of the dicationic states are found to have a very strong two-hole localization around the fluorine sites. The two electron vacancies are either localized each at a different fluorine (*two-site* states), or both at the same atom (*one-site* states) [12]. We refer to the former set of states as F₁⁻¹F₂⁻¹ states, and to the latter as F⁻² states. This localized character systematically exceeds 70% of the total two-hole weight and is on average well above 80%. The population term describing one hole on the silicon atom and one on a fluorine atom (Si⁻¹F⁻¹) is generally small and only for a few states exceeds 20%. Finally, the term describing two holes localized at the silicon center (Si⁻²) is extremely small everywhere, only for a few states reaching 2%. Because of this pronounced localized character of the charge distribution in the dicationic states of SiF₄, very different hole-hole repulsion terms arise in the double ionization energies, depending on the valence shells where the electron vacancies are located and on the one/two-site character of the states.

Accordingly, the double ionization energies appear neatly ordered in eight well separated groups, whose computed average populations are shown in Table I. The first group (labeled *A* in the table) at the low ionization energy end of the spectrum (high kinetic energy of the Auger electrons) comprises F₁⁻¹F₂⁻¹*p*⁻² states. This is followed by the states characterized by having two holes in the *p* shell of the same fluorine atom. As here the two positive charges are both confined to the same region of space, these states actually form two distinct groups, labeled *B*₁ and *B*₂, according to spin multiplicity, with all the singlets having higher energy than the triplets. The next groups of states are analogously essentially characterized as having one hole in the outer (*2p*) shell and one

TABLE I. Average two-hole populations and variance of the eight groups of computed dicationic states of SiF₄ (see text and Fig. 1). The energy ranges of the groups do not overlap. The underlined numbers represent the largest and hence most relevant numbers.

Peak	Si ⁻²	F ⁻²	Si ⁻¹ F ⁻¹	F ₁ ⁻¹ F ₂ ⁻¹
<i>A</i>	0.0052 ± 0.0058	0.0028 ± 0.0047	0.1330 ± 0.0625	<u>0.8590</u> ± 0.0705
<i>B</i> ₁	0.0047 ± 0.0026	<u>0.8451</u> ± 0.0537	0.1427 ± 0.0459	0.0075 ± 0.0053
<i>B</i> ₂	0.0071 ± 0.0057	<u>0.8308</u> ± 0.0781	0.1509 ± 0.0630	0.0111 ± 0.0105
<i>C</i>	0.0062 ± 0.0072	0.0052 ± 0.0055	0.1431 ± 0.0454	<u>0.8455</u> ± 0.0526
<i>D</i> ₁	0.0026 ± 0.0011	<u>0.8344</u> ± 0.0571	0.1575 ± 0.0532	0.0055 ± 0.0051
<i>D</i> ₂	0.0083 ± 0.0068	<u>0.8443</u> ± 0.0538	0.1244 ± 0.0283	0.0230 ± 0.0212
<i>E</i>	0.0077 ± 0.0014	0.0206 ± 0.0185	0.1567 ± 0.0101	<u>0.8150</u> ± 0.0283
<i>F</i>	0.0089 ± 0.0003	<u>0.8543</u> ± 0.0007	0.1368 ± 0.0003	0.0000

in the inner (2*s*) shell of fluorine, the two-site states (group *C*) preceding again the one-site states (groups *D*₁ and *D*₂). Here the F⁻² *p*⁻¹*s*⁻¹ states give rise to two widely separated groups, as singlet-triplet splitting is large (~10 eV) due to the presence of the inner-valence hole. Finally, the states arising from double ionization of the fluorine 2*s* inner shell appear, the one-site states (group *F*) following the two-site states (group *E*) with a gap of almost 10 eV. Without exceptions, each group comprises exactly the number of states that can be easily worked out by symmetry arguments alone, considering double ionization of four equivalent F⁻ ions.

As already described, the Si⁻² population is consistently very small in all the states. It is very important to note, however, that it is essentially distributed over the whole spectrum (see Table I) [13]. This consideration immediately acquires extreme relevance when, according to the intra-atomic nature of the Auger decay rates, one approximately identifies the Si⁻² charge distribution as the essential character determining the appearance of the states in the silicon Auger spectrum. Of course, since this character is of very small absolute magnitude, the intensity is low and the details of the spectral profile may be generally sensitive to secondary phenomena (decaying state shake up, nonadiabatic effects, etc.). It is clear, nevertheless, that the silicon spectrum must show an overall profile reflecting the distribution of dicationic states discussed above. To visualize this we have plotted in Fig. 1(a) a Gaussian convolution of the Si⁻² population of the ADC(2/2*h*) states. The full width at half maximum of the Gaussians is 2.5 eV. The figure shows very clearly the expected eight maxima in the spectrum. They are labeled as the corresponding groups of states in the table. Although by comparison with the experiment in Fig. 1(c) the lack of relaxation effects in our calculations is evident, the overall agreement between theoretical and experimental band shapes and relative intensities is striking. The theoretical peaks *B*₁ and *B*₂ obviously correspond to the second unresolved experimental band [3–5], while the highest energy peak *F* appears to be missing in the observed spectrum.

The inaccuracies in the theoretical band spacings are,

however, significant in the inner-valence region and, to conclusively verify the details of our interpretation, we should try to give consistent and reliable estimates of the effects of electron relaxation. This can be done in a well defined and unambiguous way. For the F⁻² one-site states, we can straightforwardly compare the theoretical spectrum obtained by convolution of the F⁻² population with the experimental fluorine *KVV* spectrum [1]. In this spectrum, as is clear from our discussion and the results in the table, due to the dominance of intra-atomic matrix elements, the groups of two-site states (*A*, *C*, and *E*) have virtually no intensity and the remaining groups of one-site states give rise to the typical self-imaging three-region spectrum. In the central region, the large singlet-triplet splitting of the F⁻² *p*⁻¹*s*⁻¹ states is very clearly visible. The comparison between theory and experiment shows that, relative to the main line at the low ionization energy end (due to the F⁻² *p*⁻² states, group *B*), the computed F⁻² *p*⁻¹*s*⁻¹ states are too high in energy by about 3 eV, while the F⁻² *s*⁻² states are too high by about 10 eV. The absolute shift of the F⁻² *p*⁻² states is furthermore determined to be about 10 eV by comparison with the results of the full ADC(2) calculations mentioned above. Very consistently, the latter comparison also shows that the ADC(2/2*h*) states of F₁⁻¹F₂⁻¹ *p*⁻² character are too high in energy by about 5 eV. The consistency of these two figures is shown using a theoretical analysis [14] of strongly localized (core) double holes which predicts, in second order, that the relaxation energy of one-site states is 4 times larger than that of the corresponding single holes, and thus twice that of noninteracting two-site double holes. We can then use this theory to estimate the absolute relaxation energy of the F₁⁻¹F₂⁻¹ *s*⁻² states to be 10 eV and finally that of the F₁⁻¹F₂⁻¹ *p*⁻¹*s*⁻¹ states to be 7.5 eV.

After shifting the various groups of doubly ionized states down in energy according to these precise estimates, we have redrawn the theoretical silicon spectrum of SiF₄ in Fig. 1(b). The agreement between the theoretical and experimental profiles is now excellent and even the relative energy positions of all the peaks are reproduced by our calculations with an accuracy of 1 eV. The

analysis of relaxation energy effects thus confirms beyond doubt that the peak due to $F^{-2} s^{-2}$ states is outside the energy range covered by the reported experimental spectra. We may suppose that this peak is of very problematic detection because of its low intensity (possibly redistributed over a broad energy range due to correlation effects [9]) and background noise [1,3]. Although the appearance of one-site and two-site states has been anticipated by some authors [1,3], the correct assignment of the spectrum has not been given previously.

In summary, our calculations of the silicon Auger spectrum of SiF_4 permit an unambiguous characterization of all its features and provide a definitive assignment which rules out previous interpretations. They also make evident that this spectrum is a clear-cut example of what we may define as *foreign imaging* in Auger spectroscopy: Because of ionicity and the strong space localization of the holes in the dicationic states, the spectrum is essentially deprived of information concerning the core-ionized atom itself and, in fact, hardly provides any clue about its identity. The spectrum is, instead, an astonishingly precise fingerprint of the "other" atoms present in the molecule, which fully determine the energy distribution and nature of the dicationic states. Indeed, remarkably, the central atom Auger spectrum provides more complete information on the ligands than the spectrum of the ligands themselves since, in the latter, only the doubly ionized states having both electron vacancies localized on the same atom are observed. This now well understood character of Auger spectra is expected to apply to most ionic systems [2,11] with a wide ranging degree of precision, and to be in all cases a very useful guidance for interpretation and analytic purposes. It suggests as very interesting, for example, the Auger analysis of systems with different or pairwise nonequivalent electronegative ligands, or of ionic solids, where the foreign image of several coordination spheres of counterions may be observable.

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