

Double-core-vacancy excited states in the photoabsorption spectrum of SiX_4 ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$) at the silicon 1s edge

S. Bodeur

Laboratoire pour L'Utilisation du Rayonnement Electromagnétique, Bâtiment 209 D, Université de Paris-Sud, 91405 Orsay CEDEX, France
and Laboratoire de Chimie Physique, 11, rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France

P. Millié

Département d'Etudes des Lasers et de la Physico-Chimie, Bâtiment 522, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France

E. Lizon à Lugin and I. Nenner

Laboratoire pour L'Utilisation du Rayonnement Electromagnétique, Université de Paris-Sud, 91405 Orsay CEDEX, France
and Département d'Etudes des Lasers et de la Physico-Chimie, Bâtiment 522, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette CEDEX, France

A. Filipponi

Area per la Ricerca Scientifica e Tecnologica, Trieste, Italy

F. Boscherini and S. Mobilio

Laboratori Nazionali di Frascati, Istituto Nazionale di Fisica Nucleare, via Enrico Fermi 40, 00044 Frascati, Italy
(Received 10 January 1989)

Double-core-vacancy excited states are observed in the photoabsorption spectra of gas-phase silicon molecules, SiX_4 ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$). We interpret the structures as originating from $1s2p$ and $1s2s$ electron excitations into unoccupied valence orbitals. The energies of the observed structures are found at much higher energy than the sum of individual core excitations primarily because of the Coulomb repulsion of the core holes within the silicon atom. Using Hartree-Fock calculations, we interpret the energy separation of the first doublet structure as the singlet-triplet splitting because of the $1s-2p$ ($1s-2s$) exchange term. Molecular effects due to the ligands are found in the absolute energies and in the second peak shape. We estimate the energy of the double-core ionization continua, $1s^{-1}2p^{-1}$ and $1s^{-1}2s^{-1}$, to be around 25 eV above the double excited states.

I. INTRODUCTION

Photoabsorption spectra in the x-ray region are usually interpreted in terms of a one-electron scheme; however, many-body effects are present and may account for a contribution up to a few percent of the total cross section. According to the energy of the additional electron(s) which is (are) excited, multielectron excitations occur in different regions of the main one-electron edge. In the case of valence electrons shake up, they affect the near-edge structure of the threshold, while when core electrons are excited, they occur in the region of the extended x-ray absorption fine structure (EXAFS).

Excited states with double-core vacancies have been observed in the photoabsorption spectra of rare gases¹⁻⁴ but not in gas-phase molecules. However, Cederbaum *et al.*⁵ have recently discussed double-core vacancies excited states, in a comprehensive theoretical study of several prototype hydrocarbon molecules and predicted the corresponding transitions to be a significant phenomenon, compared to single-vacancy excited states.

This is because the cross section of double core vacancies are found^{6,7} to decrease rapidly with increasing atomic numbers and this favors systems built with low- Z elements.

In condensed-phase materials, multielectron excitations have been revealed in many cases,⁸⁻¹¹ in spite of the EXAFS signal which generally hinders the double excitation part of the absorption cross section. On the other hand, EXAFS data analysis, which is of great interest for structural investigations, may be complicated by the presence of double-electron excitations. As a matter of fact, a rather high contribution of the Si $1s2p$ excitation has been evidenced⁸ in the photoabsorption cross section of amorphous hydrogenated silicon ($\alpha\text{-Si:H}$), 124 eV above the Si 1s threshold, which strongly interferes with the EXAFS signal.

In the present paper, we report experimental evidence of excited states with double-core vacancies in the 1s plus 2p shells and in 1s plus 2s shells in the photoabsorption spectra of gas-phase tetrahedral molecules SiX_4 ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$). The fact that the two holes are lo-

calized in distinct core orbitals allows the core electrons to be coupled as singlet and triplet. By means of Hartree-Fock calculations, we show that the energy separation between core electrons singlet and triplet states largely dominates any other coupling phenomenon. We show that the absolute energy of the observed multiplet components, which is much larger than the sum of the individual core excitations, is due to the Coulombic repulsion energy between the two localized holes. We evaluate also the energies of the double-ionization onsets for $1s2p$ and $1s2p$ core orbitals.

II. EXPERIMENT

Photoabsorption spectra were recorded using synchrotron radiation emitted by the (Anneau de Collision d'Orsay) (ACO) storage ring at the LURE Laboratory. The details of the apparatus and experimental procedure have been described previously.^{12,13} Briefly, a double crystal monochromator equipped with two InSb(111) crystals, provides a monochromatic photon beam with a 0.4-eV band pass at 1850 eV. The gas cell is 143 mm long and filled with the molecule of interest with a typical pressure between 3 and 20 Torr. The transmitted beam is detected with an ionization chamber. The photon energy was scanned with 0.3- or 1-eV steps depending on the width of the structure. The photon energy scale has been carefully calibrated around the Si K edge using a SiC:H solid sample as a reference.¹⁴ With this calibration, the accuracy of the photon energy scale is ± 0.5 eV. Commercially available gases have been used without further purification.

III. RESULTS AND DISCUSSION

In Fig. 1 we present the full photoabsorption spectrum of SiF_4 . We have magnified the region of interest above 1970 eV in the insert. Similar photoabsorption spectra, reduced to the region above 1960 eV, in related molecules silane (SiH_4), tetramethylsilane [$\text{Si}(\text{CH}_3)_4$], silicon tetrachloride (SiCl_4), and silicon tetrabromide (SiBr_4) are shown in Fig. 2. The most intense transition seen in Fig. 1 (which is present also in the other molecules, but not shown in Fig. 2, except SiBr_4) right below the Si $1s$ ionization edge is known to originate from a one-electron transition $\text{Si } 1s \rightarrow \sigma^*(t_2)$, where $\sigma^*(t_2)$ is one of the unoccupied antibonding ($\text{Si}-X$) valence orbital. More details on neighboring features (discrete core excited states and shape resonances as well as doubly excited states resulting from the simultaneous excitation of a core and a valence electron) can be found in separate publications.^{15,16}

The most important and new observation of the present work is the evidence of multiplet structures ~ 130 and ~ 180 eV above the Si $1s$ edge. We have reported in Table I the absolute energies of the most intense component of the multiplets labeled A_i and B . Additional shoulders and asymmetry broadening of the A_i features have been observed but have not been considered in Table I. These features originate from the double excitation of a $1s$ electron and a $2p$ electron (type A_i) and the double excitation of a $1s$ and $2s$ electrons (type B). This general assignment is based on the following reasons.

Firstly, at about the same energy above the $1s$ absorption edge where the A_i features are found, double-hole

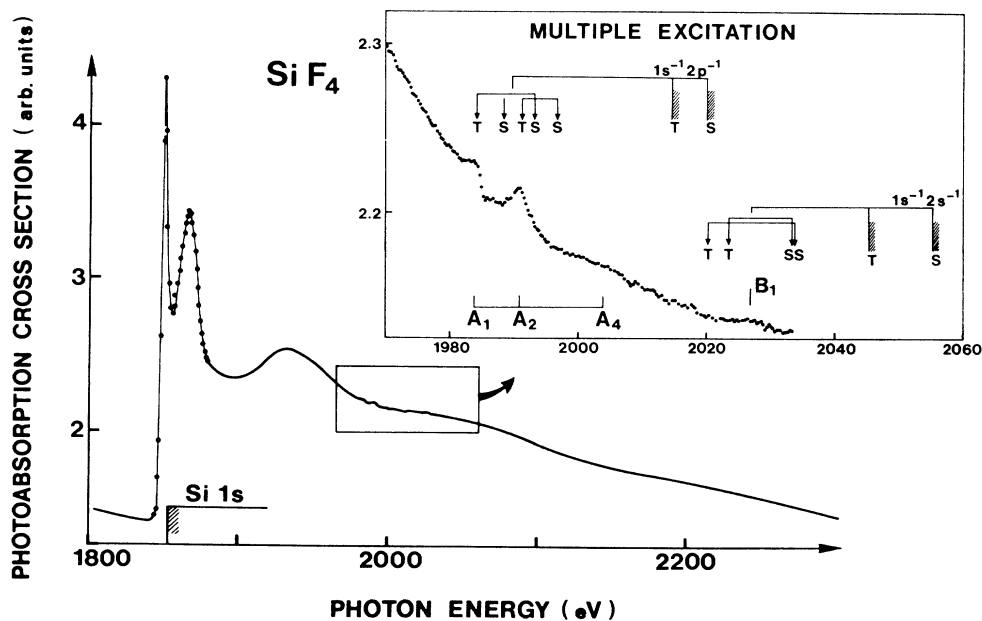


FIG. 1. Photoabsorption spectrum of SiF_4 in the 1800–2300-eV energy range. The relevant features are shown on an extended energy scale. The present calculations of the doubly excited state multiplets (strong transitions of Table IV) and the double ionization limits (Table V) are reported in scaling (-13 -eV shift) the lowest calculated transition, for $1s2p\sigma^{*2}$ configurations, to the A_1 peak. For the $1s2s\sigma^{*2}$ configurations, the scaling (-28 -eV shift) of the doubly excited states (Table IV) and the corresponding double-ionization limits (Table V) are made to the center of the B peak (see text). The notation S or T refers to the coupling of core electron in singlet and triplet. Each transition into a_1a_1 , a_1t_2 , and t_2t_2 , allowed by symmetry, is generally indicated by a singlet-triplet pair.

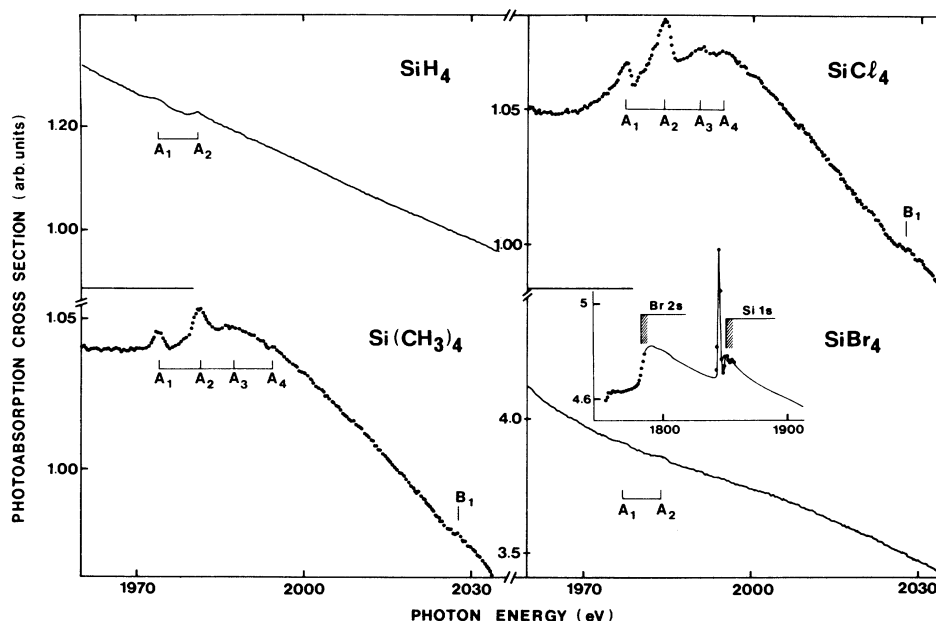


FIG. 2. Comparison of photoabsorption spectra of SiX_4 ($X = \text{H}, \text{CH}_3, \text{Cl},$ and Br) in the region above 1950 eV. The double-core vacancies are labeled A_n and B , respectively, for $1s2p$ and for $1s2s$ vacancies (see text). The relative intensity from one molecule to the other has been established by normalization to the reference peak area and the partial pressure. For SiBr_4 , the inset is shown for explaining that the low contrast originates from the superposition of the $\text{Br } 2s$ and $\text{Si } 1s$ continua.

excitations originating from $1s2p$ electrons have already evidenced in various amorphous silicon compounds.⁸ As a matter of fact, the relative energy of the mean value of the multiplet labeled A_1 and A_2 , which amounts to some 130 eV, is not far (although significantly larger) from the excitation energy for exciting a silicon $2p$ electron into one of the low-lying σ^* orbitals (106 to 109 eV in SiF_4 , Ref. 15). An even better agreement in atomic silicon is found using the $Z+1$ approximation in the presence of an additional core hole. A 122-eV value is predicted¹⁷ when a $2p$ electron is excited in the presence of a core hole. With similar considerations, the B wide feature which, in all compounds lies at ~ 45 eV above A_1 , can be assigned as due to $1s2s$ double-core excitation because the $2s$ electron binding energy is roughly 50 eV larger than the $2p$ one.

Secondly, the intensity of A_i and B features, which amounts to about 1% of the intensity of the one-electron transition, is of the same order of magnitude than previ-

ous observations.^{1-4,8-11} It also should be observed that the A and B features are much more narrower (some 3 to 4 eV full width half maximum) than shape resonances or EXAFS oscillations which extend over 10 (or more) eV. This is especially evident in Fig. 1. Such widths are comparable to those of the reference peak. This can be understood in terms of a long lifetime reminiscent of electron autoionization rather than direct ionization of the core electron. Such phenomenon has been experimentally evidenced in the SF_6 molecule excited near the sulfur $1s$ edge by Ferrett *et al.*¹⁸ In the particular case of B , its width of some 4 eV is found much wider than those of A_i , partly because the $2s$ lifetime (1.5 eV) is larger than the $2p$ one (0.1 eV). We consider that this width is too small to interpret B as a shape resonance. Nevertheless, the shape resonance associated with the ejection of the $1s$ electron in SiF_4 is found at much lower energy.¹⁵ Additional arguments for interpreting the B feature as due to $1s2s$ excitation will be given below.

TABLE I. Energies of double-core-vacancy excited states in SiX_4 ($X = \text{H}, \text{CH}_3, \text{F}, \text{Cl}, \text{Br}$). The reference peak energy [$1s \rightarrow \sigma(t_2)$] is indicated for comparison.

Molecules	$1s \rightarrow \sigma(t_2)$	Energy (eV)				
	Refs. 15 and 16	A_1	A_2	A_3	A_4	B
SiH_4	1842.5	1973.8	1980.3			
$\text{Si}(\text{CH}_3)_4$	1843.6	1974.0	1981.3	1987.3	1994.3	2027
SiF_4	1849.0	1984.0	1990.9		2013.9	2027
SiCl_4	1846.0	1977.1	1984.3	1990.6	1995.0	2028
SiBr_4	1845.0	1977.3	1984			

We now analyze in more detail the energy of the multiplets. From electric dipole selection rules within the tetrahedral symmetry group T_d the total symmetry of any of these double excited states is T_2 . Therefore, if the two core holes are found in the $1s$ and $2p$ orbitals, the three configurations $1s^{-1}2p^{-1}\sigma^*(a_1)\sigma^*(t_2)$, $1s^{-1}2p^{-1}\sigma^*(a_1)\sigma^*(a_1)$, and $1s^{-1}2p^{-1}\sigma^*(t_2)\sigma^*(t_2)$ must be considered, since the Si $1s$ and Si $2p$ have, respectively, the a_1 and t_2 symmetry and the first two empty orbitals available for the transitions have the a_1 and t_2 symmetry.^{15,16} Similarly, if the two core holes are found in the $1s$ and $2s$ orbitals, only the two configurations $1s^{-1}2s^{-1}\sigma^*(a_1)\sigma^*(t_2)$ and $1s^{-1}2s^{-1}\sigma^*(t_2)\sigma^*(t_2)$ must be considered. The other one $1s^{-1}2s^{-1}\sigma^*(a_1)\sigma^*(a_1)$ is symmetry forbidden. The total multiplicity of the final state is ruled by the total spin. Since we deal with a closed-shell molecule, i.e., a singlet initial state, we expect transitions to singlet states to be dominant. However, because of the spin-orbit matrix elements are not negligible for Si $2p$ core level, transitions into triplet states are not strictly forbidden and may be observed but as weak features.

We now evaluate in terms of the Hartree-Fock model the excitation energy $E_{ij \rightarrow kl}$ of a doubly excited state with two core vacancies i and j and two excited electrons in the unoccupied k and l orbitals. In the general case, i.e., $i \neq j$, $k \neq l$, we obtain one quintuplet, three triplet, and two singlet states. If these possible final states are built by coupling on the one hand, the i and j core electrons in singlet or triplet states and, on the other hand, the two valence electrons k and l in singlet or triplet, the matrix elements of the electronic Hamiltonian between the different final states are expressed only in terms of core-valence exchange integrals ($K_{ik}, K_{il}, K_{jk}, K_{jl}$). These integrals are very small compared to core (K_{ij}) and valence (K_{kl}) integrals and therefore are neglected. In this approximation, the transition energies are reduced to the simple formulas

$$E_{ij \rightarrow kl} = E_{i \rightarrow k} + E_{j \rightarrow l} + \mathcal{J} + \mathcal{H} \quad (1)$$

where $E_{i \rightarrow k}$ and $E_{j \rightarrow l}$ are the single-core excitation energies, \mathcal{J} is the total Coulomb term with $\mathcal{J} = J_{ij} + J_{kl} - J_{il} - J_{jk}$, and \mathcal{H} is the total exchange term, given in Table II (except for the quintuplet state which is not considered here). Notice that the $\mathcal{J}_{ij \rightarrow kl}$ term is valid for any i, j, k , and l including $i = j$ and $k = l$, whereas \mathcal{H} depends upon the coupling of the electrons in singlet or triplet. In the preceding expression, the \mathcal{J} term includes all individual J components. In contrast, in the \mathcal{H} term, the exchange between a core and a valence electron, of the K_{ik} type, are neglected. The \mathcal{J} and \mathcal{H} terms are, respectively, dominated by the J_{ij} and K_{ij} core components. The other J 's and K 's which involve the valence electrons represent only 1 or 2 eV. Taking SiF₄ for a numerical application, we have calculated the J_{ij} and K_{ij} terms for all possible vacancies in silicon (Table III). In addition, we have evaluated the $\mathcal{J} + \mathcal{H}$ term defined in Eq. (1) and added it to the experimental values of $E_{i \rightarrow k} + E_{j \rightarrow l}$. This procedure has the great advantage of including, at least partially, relaxation phenomenon. The

TABLE II. Detailed expression of the total exchange term \mathcal{H} as a function of the total multiplicity.

Configuration	Singlet	Triplet
$ii \rightarrow kk$		
$ii \rightarrow kl$	$+K_{kl}$	$-K_{kl}$
$ij \rightarrow kk$	$+K_{ij}$	$-K_{ij}$
$ij \rightarrow kl$	$+K_{kl} + K_{ij}$	$K_{kl} - K_{ij}$
	$-K_{kl} - K_{ij}$	$K_{ij} - K_{kl}$
		$-K_{ij} - K_{kl}$

results are reported in Table IV. We have also reported some qualitative indication of the line intensities on the basis of the total multiplicity. Strong transitions are expected for singlet states as stated above. Weak ones are expected for triplets allowed because of spin-orbit coupling. Very weak transitions are expected when the spin-orbit can couple only valence electrons. Notice that these qualitative considerations apply only to cases when the exchange term K_{ij} is large compared to the spin-orbit term, i.e., when the LS coupling is valid.

We have also calculated, along the same lines, the double-core ionization limit E_{ij}^{2+} . We have obtained the following formula:

$$E_{ij}^{2+} = E_i^+ + E_j^+ + J_{ij} \pm K_{ij} + C \quad (\text{singlet or triplet}), \quad (2)$$

where E_i^+ and E_j^+ are the single-ionization energies for the i and j core orbitals and C is a constant which includes relaxation and correlation effects. We have reported in Table V the corresponding double-ionization limits in taking experimental values rather than theoretical ones for single-ionization energies. This procedure has the advantage of accounting at least partly for the unknown C constant. The only previous evaluation of such E_{ij}^{2+} energies has been made by Szargan *et al.*¹⁹ In SiF₄ they found using a core-level occupation of $1s^{1.5}2p^5$ in this molecule a 2012.8-eV value resulting from the addition of the $1s$ and $2p$ binding energies calculated with the multiple scattering X_α model. Notice that this value does not include any exchange term and must be compared with the mean singlet-triplet value (2030.1 eV) extracted from Table V. This point will be discussed below.

Similar calculations give the term value $T_{ij \rightarrow kl}$ which represents the energy difference $E_{ij}^{2+} - E_{ij \rightarrow kl}$. We obtain the following formula:

$$T_{ij \rightarrow kl} = T_{i \rightarrow k} + T_{j \rightarrow l} + J_{il} + J_{jk} - J_{kl}, \quad (3)$$

where $T_{i \rightarrow k}$ and $T_{j \rightarrow l}$ are the term values for singly excited states. Notice that Eq. (3) refers to the mean term values for singlet states only. We readily observe that

TABLE III. Coulomb and exchange term energies (eV) for two core vacancies, in the silicon atom as extracted from a SCF calculation of neutral SiF₄.

Core vacancies	1s1s	1s2s	1s2p	2s2s	2s2p	2p2p
J_{ij}	229.7	61.7	65.6	43.7	44.9	50.3
K_{ij}		5.0	2.75		9	

TABLE IV. Calculated energies of the multiplet double-core-vacancy states of SiF₄ using the Hartree-Fock model.

Core vacancies	Excited electrons	Total multiplicity	$\mathcal{J} + \mathcal{H}$ (eV)	$E_i + E_j + \mathcal{J} + \mathcal{H}^a$ (eV)	Intensity
1s2p (T)	$a_1 a_1$ (S)	triplet	46.6	1996.1	weak
1s2p (S)	$a_1 a_1$ (S)	singlet	52.1	2001.6	strong
1s2p (T)	$a_1 t_2$ (T)	singlet	45.4	1997.4	strong
1s2p (T)	$a_1 t_2$ (T)	triplet	45.4	1997.4	weak
1s2p (T)	$a_1 t_2$ (S)	triplet	49.0	2001.0	weak
1s2p (S)	$a_1 t_2$ (T)	triplet	50.9	2002.9	weak
1s2p (S)	$a_1 t_2$ (S)	singlet	54.5	2006.5	strong
1s2p (T)	$t_2 t_2$ (T)	singlet	47.9	2004.0	strong
1s2p (T)	$t_2 t_2$ (T)	triplet	47.9	2004.0	weak
1s2p (T)	$t_2 t_2$ (S)	triplet	48.4	2004.5	weak
1s2p (S)	$t_2 t_2$ (T)	triplet	53.4	2009.5	weak
1s2p (S)	$t_2 t_2$ (S)	singlet	53.9	2010.0	strong
1s2s (T)	$a_1 t_2$ (T)	singlet	39.4	2048.4	strong
1s2s (T)	$a_1 t_2$ (T)	triplet	39.4	2048.4	very weak
1s2s (T)	$a_1 t_2$ (S)	triplet	43.0	2052.0	very weak
1s2s (S)	$a_1 t_2$ (T)	triplet	49.4	2058.4	very weak
1s2s (S)	$a_1 t_2$ (S)	singlet	53.0	2062.0	strong
1s2s (T)	$t_2 t_2$ (T)	singlet	42.1	2051.5	strong
1s2s (T)	$t_2 t_2$ (T)	triplet	42.1	2051.5	very weak
1s2s (T)	$t_2 t_2$ (S)	triplet	42.6	2051.6	very weak
1s2s (S)	$a_1 t_2$ (T)	triplet	49.4	2058.4	very weak
1s2s (S)	$t_2 t_2$ (S)	singlet	52.6	2061.6	strong

^aThe E_i experimental energies are extracted from Ref. 15. For $1s \rightarrow a_1$, 1846.5 eV; for $1s \rightarrow t_2$, 1849.0 eV; for $2s \rightarrow \sigma^*$, 160 eV; for $2p \rightarrow a_1$, 103.0 eV; and for $2p \rightarrow t_2$, 107.1 eV.

there is no additivity as far as the individual excitation (or ionization) energies are concerned. In the present case, the relevant J and K values which are useful for the T evaluation are reported in Table VI. Notice that the sum of $J_{il} + J_{jk} - J_{kl}$ is always positive. The term values for single excitation, known from previous experiments,¹⁵ are also reported in the same table. The resulting $T_{ij \rightarrow kl}$ terms are found to equal to 25 eV. Such values are found extremely large compared to those associated with single excitation essentially because of the large additional positive terms mentioned above.

Other ionization limits must be considered, i.e., those resulting from the excitation of a core electron plus the ionization of another like $E_{i \rightarrow k, j \rightarrow \infty}^+$. We obtain

$$E_{i \rightarrow k, j \rightarrow \infty}^+ = E_{ij \rightarrow kl} + T_{i \rightarrow k} + J_{jk} - J_{kl} . \quad (4)$$

There are many combinations leading to distinct single ionization limits. For example, taking $i = 2p$, $j = 1s$, and $k = t_2$ we find

TABLE V. Double-core ionization limits (eV) evaluated with formula (2) using experimental E_i^* values (see Ref. 15).

i	j	E_i^+	E_j^+	E_{ij}^{2+}	
				Triplet	Singlet
1s	2p	1850.5	112	2027.35	2032.85
1s	2s	1850.5	163.6	2067.8	2087.8

$$E_{2p \rightarrow t_2, 1s \rightarrow \infty}^+ = E_{2p \rightarrow t_2, 1s \rightarrow t_2} + T_{1s \rightarrow t_2} + 2.5 \text{ eV} .$$

As above for each type of transition, the two core electrons can be coupled in singlet and triplet states, increasing again the number of possible values. Although we did not report them in a table, we expect them all in between $E_{ij \rightarrow kl}$ and E_{ij}^{2+} .

We have reported in Fig. 1 the calculated values of Tables IV and V, but in retaining only the strong transitions and in scaling the energy of the lowest member of the multiplet ($1s2p \rightarrow \sigma^{*2}$) to the A_1 experimental peak. In the case of the multiplet from the $1s2s \rightarrow \sigma^{*2}$ configuration, we have scaled the mean value of the multiplet energy onto the center of the B band. The respective shifts amount to some -13 and -28 eV. They must be considered as the bad evaluation of the absolute correlation and reorganization effects inherent of the present crude model. Nevertheless, we feel that the relative values of the energies can be trusted for analyzing the gross features of the spectra. Similarly we have reported in Fig. 1 the double-ionization energies (Table V) $1s^{-1}2p^{-1}$ and of $1s^{-1}2s^{-1}$, in scaling them, respectively, by -13 and -28 eV as done for the double-core excitation energies. The other ionization continua which correspond to one ionization and one excitation, i.e., $E_{i \rightarrow k, j \rightarrow \infty}^+$, which are other convergence limits are not reported because they are too numerous.

Let us consider the results of Figs. 1 and 2, in light of the present calculations. In the first place, the number of

TABLE VI. Relevant J (eV) and term values (eV) for singly and doubly excited states in SiF_4 , using the Hartree-Fock model. The term values for singly excited states are extracted from experiment; see Ref. 15.

i	j	k	l	J_{il}	J_{jk}	J_{kl}	$T_{i \rightarrow k}$	$T_{j \rightarrow l}$	$T_{i \rightarrow l}$	$T_{j \rightarrow k}$	$T_{ij \rightarrow kl}$
1s	2p	a_1	t_2	11.88	12.89	9.22	6	3.2			24.76
1s	2p	t_2	a_1	14.0	11.5	9.22			3.5	5.5	24.88
1s	2s	a_1	t_2	11.88	12.85	9.22	6	3.6			25.11

so-called “strong” transitions in Table IV exceeds the number of observed lines. This is because we have not considered the cross sections. The corresponding calculations requires the description of the system beyond the independent-electron model and have not been done in these molecules. Nevertheless, it is reasonable to expect finding different transitions with different probabilities. Let us consider the A_i structures: If, for example, we assume that the isolated transition $1s2p \rightarrow a_1a_1$ has a negligible cross section, then the agreement between theory and experiment becomes fair and we are left with two couples corresponding to $1s2p \rightarrow a_1t_2$ and $1s2p \rightarrow t_2t_2$. Indeed, in this case the most probable transition would be $1s2p \rightarrow a_1t_2$ giving rise to A_1 and A_2 . The other transition $1s2p \rightarrow t_2t_2$ is likely responsible for the shoulder and the asymmetric broadening found on each side of the A_2 feature. Consequently, the A_1 - A_2 energy separation of 7 eV is due to the S - T separation of the $1s2p \rightarrow a_1t_2$ transition which equals at most $2K_{ij} + 2K_{kl}$. It is largely dominated by the core-electron exchange term. This explains that the A_1 - A_2 energy separation is a characteristic of the silicon atom and does not vary significantly from one molecule to the other. The molecular nature of the transitions is reduced to the K_{kl} term and is only responsible for the deviation to the $2K_{ij}$ value and the presence of the multiplet around the A_2 line. The only measurement to our knowledge which can be compared to these results was performed on the neon atom by Esteva *et al.*⁶ Here, a shape very similar to our spectra was found, with two sharp lines at the edge at a distance of 3 eV which is very close to the value of $2K_{1s2p} = 2.48$ eV which we calculate with the same approach. In contrast, when core-core vacancies are found within the same orbital ($1s1s$, $2s2s$, and $2p2p$), the K_{ij} term (Table III) does not exist. Consequently, the singlet-triplet separation is reduced to the term exchange of the valence electrons, which amounts typically to 1 or 2 eV only. This remains to be verified experimentally.

Let us analyze the other structures labeled A_3 and A_4 . From Fig. 2, one sees that they are much broader than A_1 or A_2 . They are the most pronounced in SiCl_4 and in $\text{Si}(\text{CH}_3)_4$. They have a relative energy compared to A_1 around 13 to 20 eV and this value depends on the ligand. The fact that there are no other $E_{ij \rightarrow kl}$ lines but those reported in Fig. 1, we believe that those features reflect other double excitation features described by formula (4), i.e., those which result from one-core excitation plus one-core ionization. Their relative energy with respect to

normal double-core vacancies excited states equals to $T_{i \rightarrow k} + J_{jk} - J_{kl}$, and this sum depends on the ligand. If we reduce the transitions to $(1s \rightarrow t_2, 2p \rightarrow \infty)$, $(1s \rightarrow \infty, 2p \rightarrow t_2)$, $(1s \rightarrow a_1, 2p \rightarrow \infty)$, or $(1s \rightarrow \infty, 2p \rightarrow a_1)$ including the singlet-triplet coupling of the core electrons, we expect already eight lines above the A_i features. Taking typical values of T and J in SiX_4 molecules, we expect them around 7 to 15 eV above A_i . Consequently, the interpretation of A_3 and A_4 as due to simultaneous excitation and ionization of $1s$ and $2p$ electrons is reasonable. Notice that in neon, Esteva *et al.*⁶ observed supplementary lines to the double excitation features which resemble the present observations. Although Esteva *et al.*⁶ did not interpret them in detail, they found them close to ionization limits like $1s \rightarrow \infty$, $2p \rightarrow np$, or ns .

The analysis of the B feature is more complicated. In the first place, we could not detect any multiplet within our signal-to-noise limit. Notice that the short lifetime of the $2s$ hole (and $1s$) is not favorable for detecting weak features associated to $1s2s$ double excitation. In our first analysis, we have considered that the B - A_i energy separation amounts to some 50 eV, i.e., the $2p$ - $2s$ binding energy separation and that the B width is not compatible with a multiple scattering resonance or an EXAFS oscillation. A final possibility could be the onsets of the $1s^{-1}2p^{-1}$ double-ionization continuum because the present calculations predict it not far from B (Fig. 1). We do not favor this interpretation because in a one-electron scheme analysis of photoabsorption spectra at core edges, the continuity of the oscillator strength from bound states to the continuum, combined with the short lifetime of the core hole, makes the amplitude of the ionization continuum very weak compared to the first allowed core to valence bound state. If this analogy is conserved for the double-ionization excitation spectrum, we expect the magnitude of the double-ionization continuum to have a very small amplitude compared to those of the bound states (A_i). Consequently, we are left with the interpretation of B being due to $1s2p \rightarrow \sigma^2$ double excitation.

With the preceding interpretation, we now discuss the absolute energies of these features. The calculated values of Table IV are too high in energy compared to experiment since a shift of -13 eV (or -28 eV) has been necessary to compare with the experiment. This is inherent to Hartree-Fock calculations and the fact that core-hole screening effects are not properly taken into account. Indeed, the calculation of Szargan *et al.*¹⁹ which imposes a core level occupation like $1s^{1.5}2p^5$ found a much lower

energy than the present experiment. In any case, the large experimental gap between the energy of the reference peak and the A_1 and B peaks, as seen in Table I, is not only due to the supplementary energy of exciting a $2p$ or $2s$ electron but also to the Coulombic repulsion between the core holes [the \mathcal{J} term of formula (1)]. This term amounts to more than 60 eV for $1s2p$ or $1s2s$ and reaches 223 eV for $1s1s$ (Table III). The latter value, which has not yet been confirmed experimentally, is compatible with the calculated value of 99 eV of Cederbaum *et al.*⁵ for the double $1s$ vacancies in the carbon atom of some hydrocarbons. The effect of the \mathcal{J} term is probably partly reduced because of relaxation, screening and correlation effects.

As a conclusion, we have observed double-core vacancies in photoabsorption spectra of isolated silicon compound molecules. We interpret with the Hartree-Fock model the experimental observations in terms of $1s2p$ and $1s2s$ core excitation into low-lying unoccupied valence orbitals. The almost constant energy separation between the two low-lying features A_1 and A_2 is mainly due to

the coupling of the core electrons in singlet or in triplet and is essentially independent of the chemical environment around the silicon atom. The effect of the ligands is reduced to a broadening of the bands because of the presence of several electric dipole transitions allowed in the tetrahedral symmetry group. Finally, from this work, we predict that the energies of double-core ionization limits which can be determined with photoelectron spectroscopy should be expected some 25 eV above the A_2 and B structures.

ACKNOWLEDGMENTS

We thank L. S. Cederbaum for critical comments on the manuscript. We are indebted to the Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE) staff for the general facilities and for operating the ACO storage ring. LURE is affiliated with the Centre National de la Recherche Scientifique, the Commissariat à l'Energie Atomique, and Ministère de l'Education Nationale.

¹R. P. Madden and K. Codling, *Phys. Rev. Lett.* **10**, 516 (1963).

²H. W. Schnopper, *Phys. Rev.* **131**, 2558 (1963).

³F. Wuilleumier and C. Bonnelle, *C. R. Acad. Sci., Ser. B* **270**, 1229 (1970); F. Wuilleumier, *J. Phys. (Paris)* **32**, C-488 (1971).

⁴R. D. Deslattes, R. E. La Villa, P. L. Cowan, and A. Henis, *Phys. Rev. A* **27**, 923 (1983).

⁵L. S. Cederbaum, F. Tarantelli, A. Sgamellotti, and J. Schirmer, *J. Chem. Phys.* **86**, 2168 (1987).

⁶J. M. Esteve, B. Gauthé, P. Dhez, and R. C. Karnatak, *J. Phys. B* **16**, L263 (1983).

⁷J. P. Briand, P. Chevalier, A. Chetioui, J. P. Rozet, M. Tavernier, and A. Tonati, *Phys. Rev. A* **23**, 39 (1981); S. I. Salem and A. Kumar, *J. Phys.* **19**, 73 (1986).

⁸A. Filipponi, E. Bernieri, and S. Mobilio, *Phys. Rev. B* **38**, 3298 (1988).

⁹S. I. Salem and B. Dev, *Phys. Rev. A* **22**, 2679 (1980).

¹⁰S. I. Salem, D. D. Little, A. Kumar, and P. L. Lee, *Phys. Rev.*

A **24**, 1935 (1981).

¹¹M. Deutsch and M. Mart, *Phys. Rev. A* **29**, 2946 (1984).

¹²M. Lemmonier, O. Collet, C. Depautex, J. M. Esteve, and D. Raoux, *Nucl. Instrum. Methods* **152**, 109 (1978).

¹³S. Bodeur and J. M. Esteve, *Chem. Phys.* **100**, 415 (1985).

¹⁴C. Sennemaud (private communication).

¹⁵S. Bodeur, I. Nenner, and P. Millié, *Phys. Rev. A* **34**, 2986 (1986); **37**, 644(E) (1988).

¹⁶S. Bodeur, P. Millié, I. Nenner, M. Benfatto, and C. R. Natoli (unpublished)

¹⁷S. Mobilio (private communication).

¹⁸T. A. Ferrett, D. W. Lindle, P. A. Heimann, H. G. Kerkhoff, U. E. Becker, and D. A. Shirley, *Phys. Rev. A* **34**, 1916 (1986).

¹⁹R. Szargan, A. Meisel, E. Hartmann, and G. Brunner, *Jpn. J. Appl. Phys.* **17**, Suppl. 17-2, 174 (1978).