

## Normal and resonance $LVV$ Auger spectra of gas-phase $\text{SiCl}_4$ molecules

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Si  $LVV$  and Cl  $LVV$  Auger spectra of  $\text{SiCl}_4$  have been studied in the gas phase with the use of different photon energies from synchrotron radiation or an electron beam, either to ionize  $2p$  electrons or to excite them selectively to unfilled molecular or Rydberg orbitals. In the case of resonance excitation, the kinetic energies of the main Auger peaks have been found to depend clearly on the antibonding molecular orbital to which the  $2p$  electrons have been excited. For the excitation at the first strong resonance maximum, the Si  $LVV$  kinetic energies have been found to be 5.2 eV higher than the energies of the corresponding peaks in the normal Auger spectrum. This shift compares with 7.5 eV for the equivalent excitation in  $\text{SiF}_4$ . In the case of Cl, the spectator Auger spectra show very high intensity and broad structureless peaks. Valence-band intensities do not vary greatly at either the Si  $2p$  or Cl  $2p$  edges, showing that the spectator Auger process is the major decay mechanism for the resonantly excited core hole.

### I. INTRODUCTION

The Si  $2p$  absorption spectra of gaseous  $\text{SiCl}_4$  has been studied, e.g., by Fomichev *et al.*,<sup>1</sup> Zimkina *et al.*,<sup>2</sup> Pavlychev *et al.*,<sup>3</sup> and very recently with high resolution by Bozek *et al.*<sup>4</sup> Analogously, with the absorption spectrum of  $\text{SiF}_4$ , the spectrum of  $\text{SiCl}_4$  also shows strong maxima below the Si  $2p$  ionization threshold. These correspond to excitations of the Si  $2p$  electrons to unfilled molecular and Rydberg states, but the spectrum has not been rigorously assigned as yet. The purpose of this work has been to study in detail the normal Auger spectrum following the ionization in  $2p$  levels, and especially the resonance Auger spectra and its energy dependence due to corresponding excitations to the different resonance states below the Si  $2p$  and Cl  $2p$  ionization thresholds. Previously<sup>5</sup> we investigated resonance Auger spectra of  $\text{SiF}_4$  and this study is intended to continue our efforts to understand resonance Auger spectra of free molecules.

### II. EXPERIMENTAL

The measurements of the synchrotron radiation excited spectra were carried out using the Canadian synchrotron Radiation Facility situated at the 1-GeV Aladdin storage ring in Stoughton, Wisconsin. Preliminary measurements were done also at the Tantalus storage ring. The much higher photon flux of the Aladdin storage ring in the energy range of this study (100–230 eV) has made it possible to measure the spectra with a much smaller photon bandwidth and with improved counting statistics. The beamline uses the Grasshopper Mark-IV monochromator equipped with a 1200-groove/mm holographic grating from JY Inc., and the electron spectra were taken with

the Leybold-Heraeus electron spectrometer, applying a constant 100 eV pass energy. The electron spectrometer contribution to the observed Auger line widths [full width at half maximum (FWHM) 2–3 eV] was a minor factor. The rather large widths in these molecular Auger spectra are mainly caused by the overlap of many close-lying line components. For the widths of the valence-band photolines (1.0 eV) the main contribution arises from the photon bandwidth, about 0.8 eV at the used 150  $\mu$  slit widths at 100 eV photon energy. Again the electron spectrometer broadening (0.5 eV) is a minor factor.

The electron beam excited normal Si  $LVV$  Auger spectra were taken at the University of Oulu using the high-resolution CMA electron spectrometer. The spectra were excited by 3-keV electrons and the primary beam current was about 1 mA. The pressure of the target gas in the effective source volume is approximated to be about  $10^{-3}$  torr. This is low enough that the inelastic scattering processes of emitted electrons from the main peaks do not contribute significantly to the intensity at lower energies.

### III. RESULTS AND DISCUSSION

#### A. Normal Auger spectra of Si

The high-resolution absorption spectrum<sup>4</sup> of gaseous  $\text{SiCl}_4$  depicted in Fig. 1 shows prominent peaks below the ionization threshold of the Si  $2p$  levels. The first doublet, consisting of the  $2p$  spin-orbit components between 104 and 105 eV [1,1'; Fig. 1(b)], is most intense and the other strong doublets are around 106 (2,2',3,3') and 110 eV (6,6'). The last doublet partially overlaps with the ionization thresholds at 110.2 and 110.8 eV for Si  $2p_{2/3}$  and  $2p_{1/2}$ , respectively.<sup>4</sup> Above the threshold, the spectrum

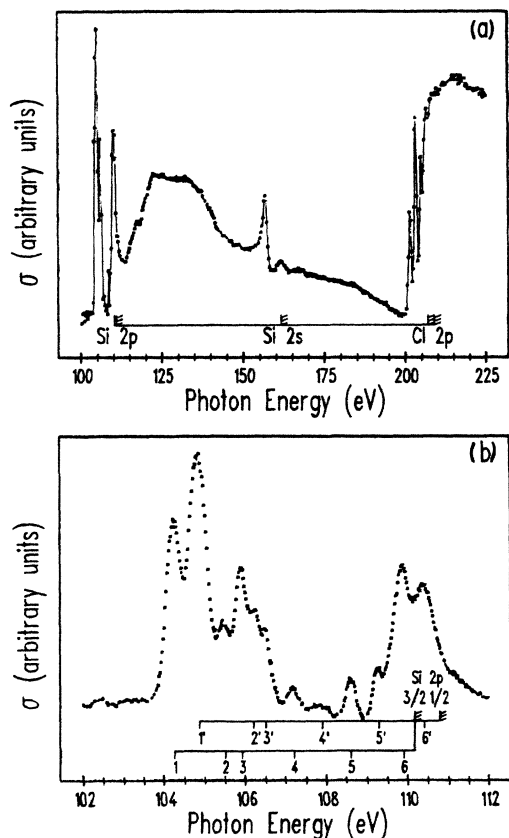


FIG. 1. Absorption spectrum of  $\text{SiCl}_4$  from Ref. 4.

shows intense shape resonances, although not as intense as those for  $\text{SiF}_4$ . In order to study the kinetic energy shifts of the spectator Auger spectra relative to the normal Auger spectrum, the normal Auger spectrum was measured by the use of 125 eV photon energy which is well above the  $2p$  ionization thresholds. For comparison, the Si *LVV* spectrum was also taken using excitation by 3-keV electrons. These normal Auger spectra are shown in Fig. 2. The main features of the spectra are very similar. The spectra show two prominent doublets around 75 eV and 65 eV kinetic energies and some weaker structures below 60 eV. It is obvious that the highest kinetic energy doublet corresponds to Auger transitions of the *LVV* type where both the final-state holes are in the outer valence orbitals with significant Si character. As for  $\text{SiF}_4$ , the doublet structure again<sup>5,6</sup> corresponds to the cases where the two final-state holes are located in the same or different Si-Cl bonding orbitals. The higher interaction energy between the holes located in the same bonding orbitals corresponds to the lower kinetic energy peak. The least-squares fitting of the experimental spectrum gives the separation of 2.7 eV between the components. The lower doublet around 65 eV is correlated to the cases where one of the final-state holes is in the valence levels and the second hole is in deeper levels, consisting mainly of Cl  $3s$  atomic orbitals, but having also some Si character. In the photoelectron spectrum this "Cl  $3s$ " peak has the binding energy of 24.6 eV which is about 10 eV below

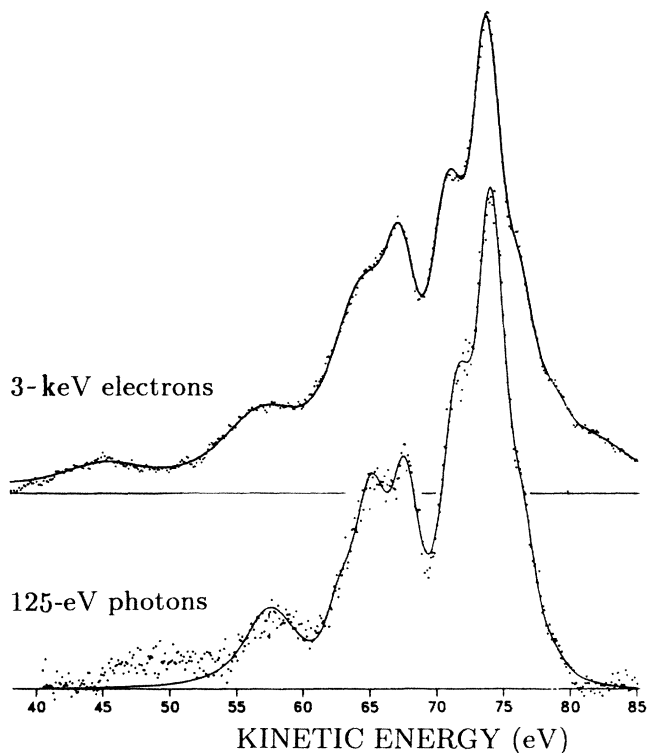


FIG. 2. Si *LVV* normal Auger spectra from  $\text{SiCl}_4$  molecules excited by 125-eV photons and 3-keV electrons.

the main valence levels. This Auger doublet has a kinetic energy 6.5 eV lower than the main doublet, comparing favorably with the corresponding binding energies. The structure below 60 eV should then be associated with transitions where both final-state holes are in Cl  $3s$  levels.

### B. Resonance Auger spectra of Si

We like to discuss decay processes after resonant excitation of a core electron in terms of the Auger process. The alternative method of consideration can be based on the photoemission and satellite photoemission phenomena. We call resonance Auger spectra electron spectra emitted after resonant excitation of a core electron in order to distinguish them from the normal Auger spectra which follow the ionization of the core level.

In the simplest model, the resonance Auger spectra are usually thought to be created by two main types of processes. In the first one, the excited  $2p$  electron directly takes part in the decay (autoionization) process and the molecule has the same one-hole final states as after the direct photoemission. This participating Auger process can thus manifest itself as enhanced and possibly changed relative intensities of the photoelectron line components at resonance photon energies. The second decay channel, in which the excited electron remains as the spectator during the Auger process, creates final states identical with normal photoemission and a simul-

taneous shakeup process. This type of event is often called the spectator Auger process. Recent studies<sup>7-11</sup> have, however, shown that other decay channels are also significant. Especially shakeup and shakeoff processes associated with the emission of the resonance Auger electron have been found to be strong.

The participating process should mainly affect the relative intensities of line components in the valence band, and the spectator events should change the structure of the photoelectron spectrum some eV below the valence band. In order to observe these changes, outer level photoelectron spectra up to binding energies of 55 eV were taken with photon energies 100, 103.8, 104.5, 105, 105.5, 106, 106.6, 109, and 110.5 eV mapping the range of the absorption resonances. The series of these spectra are shown in Figs. 3 and 4.

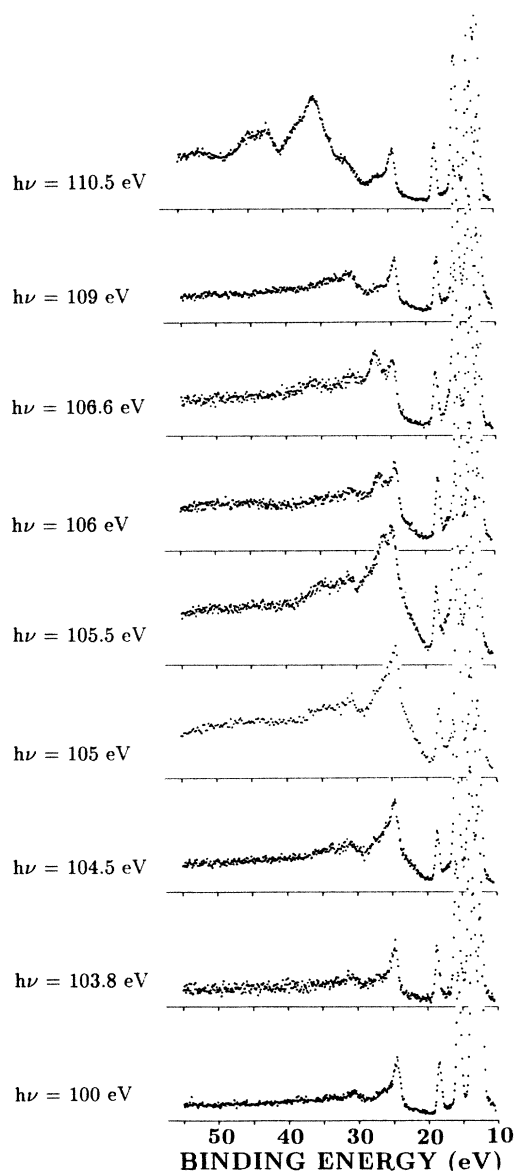


FIG. 3. Electron spectra of  $\text{SiCl}_4$  in the binding-energy range 10–55 eV of the participating and spectator resonance Auger lines taken with different photon energies and showing the appearance of resonance Auger features.

The spectrum taken with 100-eV photons, well below the resonance excitation energies, represents the normal photoelectron spectrum to be used as the reference spectrum for the others. The outer valence-band region,  $E_B = 10\text{--}20$  eV, manifests itself as four dominating peaks in the spectrum, rather analogous to the  $\text{SiF}_4$  valence-band spectrum. The peaks arise from the valence orbitals<sup>12</sup>  $2t_1$ ,  $8t_2$ ,  $2e$ ,  $7t_2$ , and  $7a_1$  with binding energies of 12.1, 13.0, 13.5, 15.4, and 18.2 eV, respectively. The  $8t_2$  and  $2e$  orbitals are so close to each other that it is not possible to separate them with the applied monochromator and electron spectrometer resolutions. The relative intensities of these four lines have been determined by fitting the spectra (Fig. 4) with the least-squares-fitting program package<sup>13</sup> CRUNCH and the results are plotted in Fig. 5. A smooth background has been subtracted from

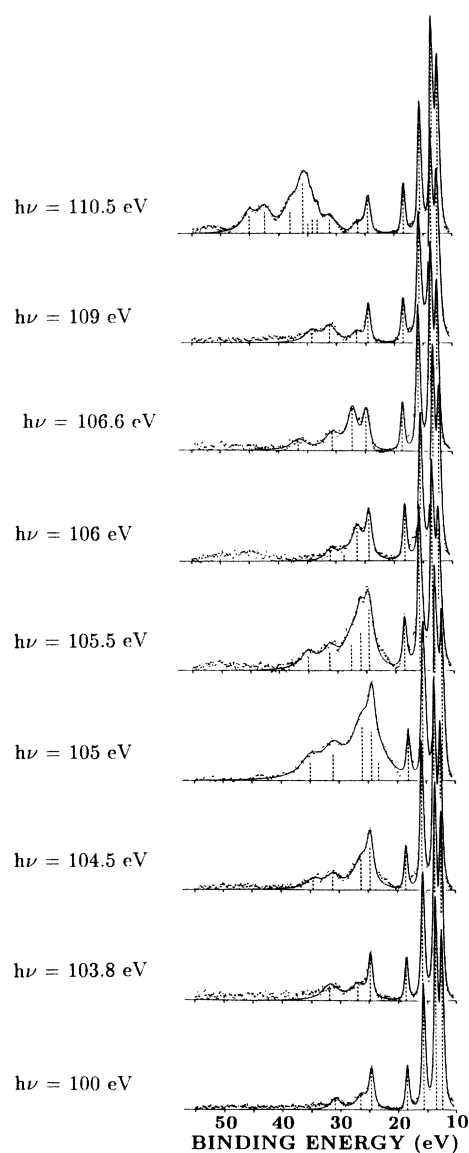


FIG. 4. Spectra of Fig. 3 fitted by the line components shown by dashed vertical lines. Smooth background represented by third-order polynomials has been subtracted from the original spectra.

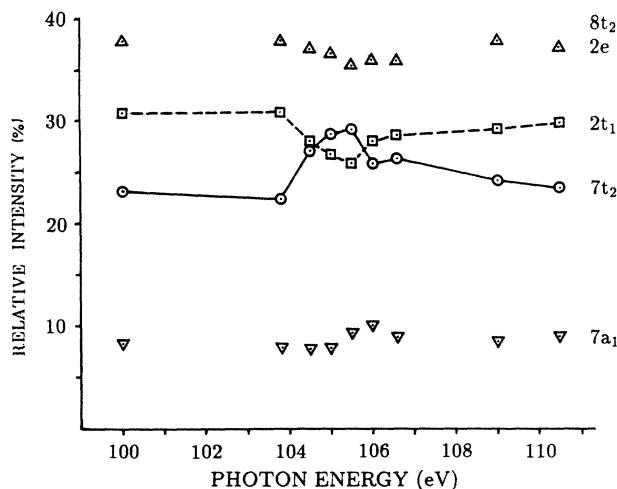


FIG. 5. Relative intensities of valence-band line components as the function of photon energy around Si  $2p$  resonance excitation energies.

the spectra in the fitting procedure.

From the results of Fig. 5 it can be seen that the relative intensities of the peaks do not show very prominent variations as the photon energy goes through the resonances. Only the  $7t_2$  peak clearly resonates at 105.5 eV, having its maximum relative intensity of 29.2% of the sum of intensity of the four peaks, while its intensity is about 23% below and above the resonances. The second obvious feature is that the  $2t_1$  peak shows just the opposite behavior having its intensity minimum at  $\sim 105.5$  eV. Clearly, apart from autoionization between 104.5 and 106 eV, the autoionization process is not an important decay process. A similar result was found<sup>5</sup> for  $\text{SiF}_4$  but de Souza *et al.*<sup>14</sup> found that autoionization was significant for  $\text{SiH}_4$ .

Below the outermost valence band, the spectrum shows Cl  $3s$  at the binding energy of 24.6 eV and some other weaker structures. The range around the Cl  $3s$  peak is where the effects of the spectator Auger process should be revealed. This can be seen clearly from the spectra taken at higher photon energies. Already at 104.5 eV photon energies, features around the Cl  $3s$  peak grow clearly relative to the valence band (Figs. 3 and 4) and the effect becomes most prominent at photon energies of 105 and 105.5 eV.

The absorption spectrum<sup>4</sup> in Fig. 1 shows that at photon energies around 105 eV excitations to the states corresponding to the strongest absorption peaks 1 and 1' take place. This excited state decays mainly by the spectator Auger process, giving the large peak with kinetic energy of 79.4 eV (binding energy of 26.6 eV). The corresponding energy of the large peak in the normal Auger spectrum is 74.2 eV (Fig. 2). Thus the shift is 5.2 eV. At photon energies of 104.5 and 105 eV the resonance features almost completely coincide with the Cl  $3s$  peak but become more obvious at photon energies 105.5, 106, and 106.6 eV. The intensity of the spectator Auger structures reaches its maximum at 105.5 eV, but still at 106 and 106.6 eV photon energies, clear resonance peaks can

be seen. Inspection of the spectra taken by 106 and 106.6 eV shows that the relative intensity of the spectator Auger peaks is clearly higher for 106.6 eV photon energy indicating more effective excitation to states corresponding to features 2'–3' in the absorption spectrum. At 109 eV photon energy a new peak appears at a lower kinetic energy of 77.9 eV (a shift of 3.7 eV). We interpret this to correspond to the excitation to peaks 5 and 5' in the absorption spectrum. At 110.5 eV photon excitations to states ( $5', 6, 6'$ ) just below the ionization threshold of 110.2 and 110.8 eV in absorption spectrum are at a maximum, giving an intense new structure whose strongest peak has the kinetic energy of 74.6 eV, which is only very slightly (0.4 eV) higher than the energy of the main peak in the normal Auger spectrum. Further comparison with the normal Auger spectra of Fig. 2 shows that the shape of this spectator Auger spectrum excited by 110.5-eV photons is very much the same as that of the normal Auger spectrum. Only the kinetic energies are slightly higher as expected. Also other spectator Auger spectra, e.g., at photon energy 105.5 eV show in addition to the main "peak" weaker "double peak" structure at lower kinetic energies analogously with the normal Auger spectra. This supports Auger-type point of view that molecular spectator Auger spectra can be considered in the first approximation as shifted Auger spectra with about the same relative intensities of the peaks.

The detailed interpretation of these shifts must await accurate molecular orbital (MO) calculations to interpret the pre-edge absorption spectrum and calculation of the expected shifts for different antibonding and Rydberg spectator electrons. Very preliminary interpretations of the absorption pre-edge structure have been given previously.<sup>1,15</sup> However, a comparison of the  $\text{SiCl}_4$  and  $\text{SiF}_4$  Auger shifts is informative. In our previous  $\text{SiF}_4$  paper,<sup>5</sup> the Auger shift for the lowest-energy pre-edge peak at 106 eV was 7.5 eV, while the shift for the highest-energy pre-edge peaks at  $\sim 111$  eV was 2.7 eV, giving range of 4.8 eV. These two peaks were assigned as  $\text{Si } 2p \rightarrow \sigma^*(3s)$  and  $\text{Si } 2p \rightarrow \text{Si } 3d$ , respectively. Coincidentally, the range of shifts for  $\text{SiCl}_4$  is also 4.8 eV, although the absolute values are  $\sim 2$  eV smaller. These results show rather conclusively that the excitation just below threshold in both molecules is not  $\text{Si } 2p \rightarrow \text{Si}$  Rydberg (such as  $\text{Si } 3d$ ) because the shifts should be very similar for both molecules. This agrees with a recent suggestion by Bodeur *et al.*<sup>15</sup> that transitions to Rydberg levels are not important. The low-energy resonances in  $\text{SiCl}_4$  and  $\text{SiF}_4$  probably correspond to the equivalent transition to a  $\sigma^*$  orbital [such as the  $\sigma^*(3s)$ ] in both cases. The larger shifts for  $\text{SiF}_4$  are probably due to the fact that the antibonding orbitals in  $\text{SiF}_4$  have a larger Si character than in  $\text{SiCl}_4$ .

### C. Cl Auger spectra

The absorption spectrum [Fig. 1(a)] shows strong pre-edge resonances also in the vicinity of the Cl  $2p$  ionization thresholds. In order to study the corresponding resonance Auger spectra of Cl we have measured the extended low-resolution valence-band spectra at photon energies of 190 eV, which is well below any resonance ab-

sorption peaks, and at resonance energies 203.5, 205.5, and 207.5 eV. The spectra are shown in Fig. 6 after a five-point smoothing with the Savitzky-Golay procedure. For comparison purposes, the normal Auger spectrum shown in Fig. 7 was measured using 230 eV photon energy.

The most striking feature in the spectra of Fig. 6 is the very high intensity of the spectator Auger structures, at resonance energies 203.5, 205.5, and 207.5 eV. The spectator Auger features are more intense than the outermost valence band. Both the Cl  $L_{VV}$  normal and spectator Auger spectra are characterized by very broad features. Only in the normal Auger spectrum (Fig. 7) can some sharper peaks be seen on the top of a broad peak [ $\sim 6$  eV (FWHM)]. A further pronounced feature is that the spectator Auger "peak" is rapidly getting broader [from 4 to 10 eV (FWHM)] on going to higher photon energies.

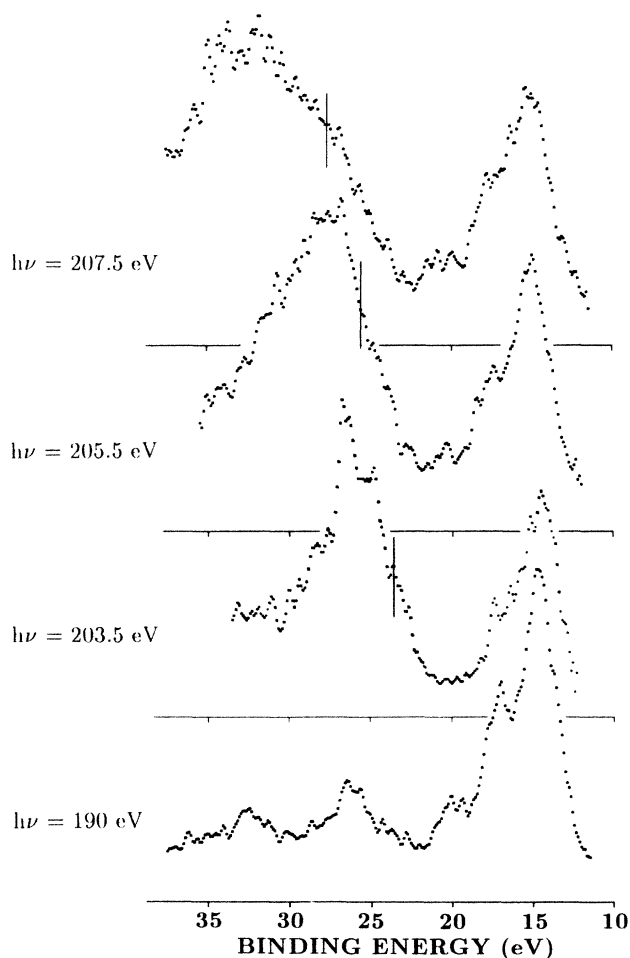


FIG. 6. Electron spectra of the valence-band region ( $E_B = 12-36$  eV) from  $\text{SiCl}_4$  taken with photon energies 190, 203.5, and 207.5 eV. The photon energy of 190 eV is below the Cl  $2p$  pre-edge resonances whereas energies 203.5, 205.5, and 207.5 eV are resonance excitation energies creating strong spectator Auger spectra. Slight smoothing over five points has been applied to the data.

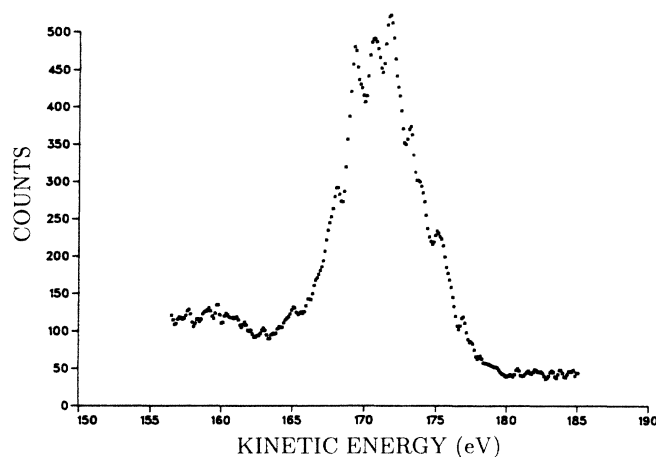


FIG. 7. Cl  $L_{VV}$  normal Auger spectrum excited by 230-eV photons.

The kinetic energy shifts relative to the normal Auger spectrum are rather difficult to determine but roughly the spectrum excited by 203.5-eV photons has shifted 6.5 eV to higher kinetic energies. The shift is almost the same for 205.5 eV, and about 4 eV for 207.5-eV photon excitation. As mentioned already, these shift values are only tentative due to difficulties in locating the very broad peaks.

The broadening of the observed spectator Auger structure can be at least partly explained by the relatively broad photon bandwidth (2 eV) and by the structure of the absorption spectrum. At the photon mean energy of 203.5 eV, only the first sharp resonances are covered which manifests itself as a relatively narrow spectator peak. Actually this peak is narrower than the normal Auger peak. At higher photon energies, the bandwidth covers the more extended portion of the very fast increasing continuous part of the absorption spectrum. These excitations decay emitting Auger electron with lower kinetic energies. Thus the spectator Auger structure gains more intensity on its low-energy side appearing as the clear broadening of the "peak." The high-energy part remains almost unchanged, as can be seen from the vertical lines in Fig. 6 drawn to show the position of the 180 eV kinetic energy.

In order to study the relative strength of the participating Auger or autoionization process and its effects on the relative intensities of outer valence-band lines, the binding-energy ranges from 10 to 21 eV were measured using the same photon energies with higher monochromator resolution (1 eV). The fitted spectra are shown in Fig. 8 and the relative intensities of the lines as a function of photon energy are shown in Fig. 9. It can be seen that the variations in the relative intensities of the valence-band line components are very small, indicating that the spectator resonance Auger process is the dominating decay channel by far. It is also interesting to note that the relative valence-band intensities are very similar at  $\sim 200$  eV and  $\sim 100$  eV photon energies (Figs. 5 and 9).

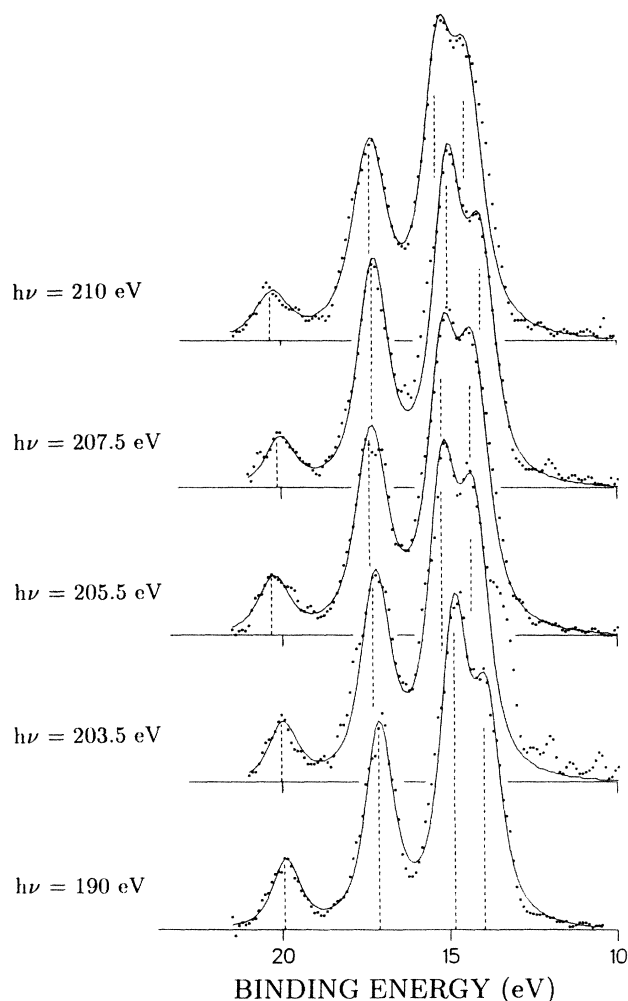


FIG. 8. Outer valence-band spectra taken below resonance energy of 190 eV and by the resonance energies.

#### IV. CONCLUSIONS

The Auger spectra of  $\text{SiCl}_4$  molecules have been studied using selective excitation of Si  $2p$  or Cl  $2p$  electrons to

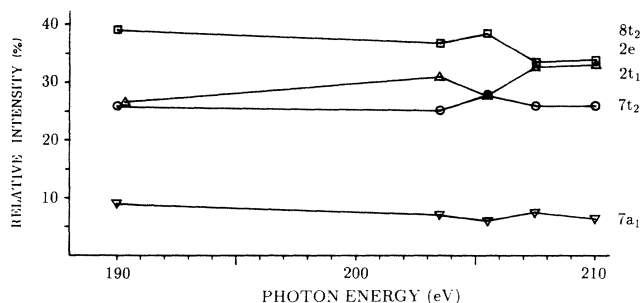


FIG. 9. Relative intensities of valence-band line components for the photon energies around Cl  $2p$  resonance excitation energies.

unfilled molecular orbitals. The kinetic energy shifts of 5.2, 3.7, and 0.4 eV for the main peak (relative to the normal Auger spectrum) have been found for the resonance excitations of Si  $2p$  electrons to the states which are 5.9, 4.3, and 0.3 eV below the  $2p$  ionization thresholds. The variations of the relative intensities of the valence-band line components have been found to be rather small for resonance excitations of Si  $2p$  electrons and still smaller for Cl  $2p$  excitations, indicating that the spectator resonance Auger decay channel dominates. The same conclusion is supported also by the very high intensity of the broad spectator Auger structures for Cl.

#### ACKNOWLEDGMENTS

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