

Decay processes after resonant excitation of S 2p and F 1s electrons in SF₆ molecules

G. M. Bancroft and K. H. Tan

*Department of Chemistry and Centre for Chemical Physics, University of Western Ontario, London, Ontario, Canada N6A 5B7
and Canadian Synchrotron Radiation Facility, Synchrotron Radiation Center, University of Wisconsin-Madison,
Stoughton, Wisconsin 53589*

O.-P. Sairanen, S. Aksela, and H. Aksela

Department of Physics, University of Oulu, SF-90570 Oulu, Finland

(Received 28 August 1989)

S *LVV* and F *KVV* resonance Auger spectra have been studied from SF₆ gas-phase molecules using selective excitation of S 2p and F 1s electrons to different resonance states with high-resolution monochromated synchrotron radiation for S 2p and with lower resolution for F 1s. The normal Auger spectra were measured using both synchrotron radiation and high-energy electron-beam excitation. The kinetic energy shift of the resonance S *LVV* and F *KVV* Auger spectra (with a spectator electron in the 6a_{1g} orbital) relative to the normal Auger spectra are 11.0 and 8.0 eV, respectively. These values, in comparison to the 7.5 eV for the Si *LVV* Auger shift in SiF₄, are discussed. The spectator Auger process is the dominating decay channel, but, in the case of S, the participating or autoionization decay channel is also found to be important in enhancing the intensity of bonding levels such as the 4t_{1u} level in the outer valence band and especially the 4a_{1g} and 3t_{1u} inner valence-band levels with significant sulfur character. No significant changes in Auger or valence-band spectra were seen at intense above-edge resonances, such as the e_g resonance at 196-eV photon energy.

I. INTRODUCTION

Synchrotron radiation has recently provided an unique tunable source to selectively excite core-shell electrons to different bound valence or Rydberg states or into different "resonance" states in gas-phase atoms¹⁻⁸ and molecules.⁹⁻¹⁵ Electron spectroscopy has been used successfully to observe the kinetic energy distribution of electrons (outer valence, inner valence, and Auger) emitted in the decay process.¹⁻¹⁶ Such spectra are important not only for understanding the decay process(es), but also for understanding both the nature of core-level resonances (both above and below threshold), and the excited-state electronic structure of atoms and molecules.

In very recent studies of the decay processes in the rare gases¹⁻⁸ and molecules⁹⁻¹⁶ two major deexcitation processes have usually been identified (see Fig. 1, Ref. 13 for a pictorial representation). In the first process, the excited electron remains as the passive spectator when the core hole is filled by another outer-shell electron and a second electron is emitted. This is called the spectator resonance Auger or, in short, the resonance Auger process. The second possibility is that the excited core electron participates directly in the emission process which is then called the participating Auger process. The latter is identical with the autoionization phenomenon appearing commonly in outer-shell ionizations. Recent studies show that the resonance Auger process is dominant in the decay, although the participator process has been observed in SiCl₄,^{12,13} for example. The shifts of the resonance Auger spectra relative to the normal Auger spectra are readily observed in both atoms and molecules (and

readily calculated in atoms^{2,3,7,8}), and these shifts are characteristic of the antibonding or Rydberg orbital in which the spectator electron resides.^{2,3,11,12}

In addition to the two dominant processes, the shakeup of the spectator electron can be important^{2,3,7} (and even dominant⁷) in atoms, but this effect has not been observed undisguised in the spectra of molecules. This probably arises from the more complex spectral structure of the molecular Auger spectra appearing usually as many overlapping rather broad line components. Very recently, many-electron effects have been identified in above-edge resonances on the S 1s and 2p levels in SF₆,^{11,14} but this interesting effect has not been further characterized in the electron spectra. In the hydride molecules, a new decay channel has recently been identified:¹⁷⁻¹⁹ the fast dissociation of the molecule followed by the resonance Auger process in the excited fragment.

We have undertaken a detailed study of the normal S *LVV* and F *KVV* Auger spectra of SF₆, and the valence band and resonance S *LVV* and F *KVV* Auger spectra following selective excitation of the S 2p and F 1s electrons to different resonances below and above threshold (see Fig. 1 for the S 2p absorption spectrum which shows the rich resonance structure).²⁰⁻²⁵ High monochromator resolution was used for S spectra but for intensity reasons we had to use low resolution for F 1s spectra. This study had three major objectives. First, it was our intention to characterize quantitatively the decay processes after excitation of the S 2p electron to the 6a_{1g} orbital below threshold (Fig. 1). For example, we wanted to show whether the spectator or participator process is dominant, which participator channel(s) are important, and

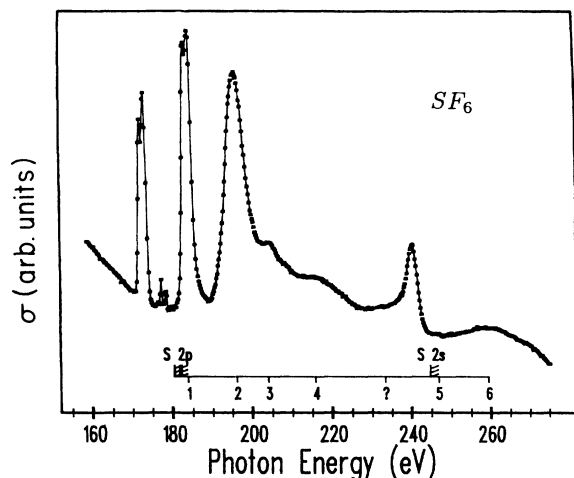


FIG. 1. Absorption spectrum of SF₆ from Ref. 20 showing strong preedge resonances and shape resonances above S 2*p* ionization limits.

rationalize why they are important, determine the shift of the resonance Auger spectra relative to the normal Auger spectra, and compare these results with the recent results on other polyatomic molecules such as SiF₄ and SiCl₄. A very recent low-electron-energy-resolution study of just this decay process in SF₆ (Ref. 14) showed new satellites in the outer valence region, but could not address any of the above points.

Second, we also wanted to obtain the resonance Auger shift after excitation of the F 1*s* electrons to the 6*a*_{1g} orbital, and compare this shift with that obtained for the S 2*p* excitation. Third, following the interesting recent observation of Ferrett *et al.*¹⁴ of many-electron effects contributing to the *e*_g resonance at 195 eV (no. 2 in Fig. 1), we wanted to examine the electron spectra in detail to see if we could detect the decay processes resulting from the shakeup or many-electron states above the S 2*p* threshold.

II. EXPERIMENT

The experimental measurements of this study with synchrotron radiation were carried out using the Canadian Synchrotron Radiation Facility at the Aladdin storage ring in Stoughton, Wisconsin. The beamline and its Mark IV Grasshopper monochromator have been described in more detail elsewhere.^{26,27} The Leybold-Heraeus LHS-11 system was used as the electron spectrometer. The analyzer is mounted at the true magic angle ($\theta_x = \theta_y = \theta_z = 54.7^\circ$) so that the electron intensities are independent of the angular parameter and of the polarization of the photon beam. The analyzer was used in the constant pass energy mode with 50-eV pass energy. The electron spectrometer contribution to the observed widths was less than 0.4 eV. A 1200 groove/mm or 900 groove/mm holographic grating was used in the Grasshopper grazing incidence monochromator. The to-

tal (photon + electron spectrometer) resolution for most spectra was ~ 0.7 – 0.9 eV, enabling us to resolve all valence-band peaks. The gaseous SF₆ was introduced into the interaction region of the spectrometer through a 30 micron capillary. Normal S LMM and F KLL Auger spectra were also measured using electron impact excitation at the University of Oulu by means of a high-resolution cylindrical mirror-type electron spectrometer.²⁸ The energy resolution of this spectrometer was better than 0.1% from the unretarded kinetic energy of Auger electrons. The impact energy of the primary electrons was 3 keV and the primary beam current about 1 mA. The sample gas pressure in the gas cell was estimated to be about 10^{-4} torr. The energy calibration of the Auger spectra was based on the known kinetic energies of Ne KLL (¹D₂) and Ar L₃M_{2,3}M_{2,3} (¹D₂) lines.²⁸

III. RESULTS AND DISCUSSION

A. Normal S LVV and F KVV Auger spectra of SF₆

In order to study the resonance Auger spectra, and the shifts of the spectator Auger spectra relative to the normal Auger spectra, the normal Auger spectra must be recorded. The normal S LVV and F KVV Auger spectra, excited both by synchrotron radiation well-above threshold and 3-keV electrons, are shown in Figs. 2 and 3. Both the photon-excited and electron-excited spectra (Figs. 2 and 3) are qualitatively similar, basically consisting of two broad peaks (> 5 eV width). The electron-excited spectra show more fine structure, at least partly due to better statistics and resolution.

As expected from the rich valence-band spectrum (Fig. 4) which contains six outer valence peaks and several overlapping inner valence peaks,²⁰ the Auger spectra are very complicated because of the many overlapping components. All the possible Auger energies and intensities

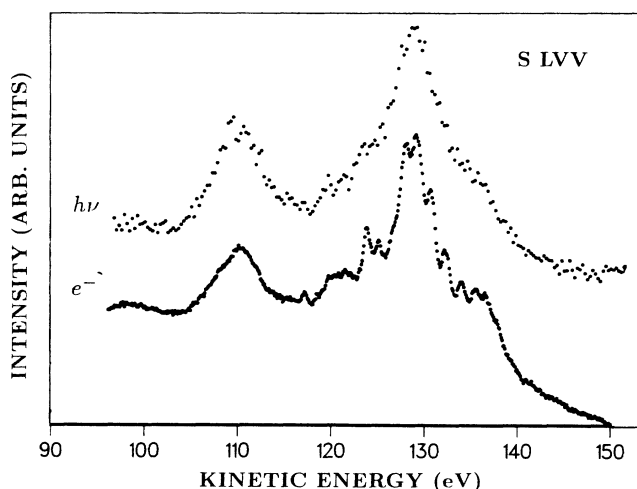


FIG. 2. Normal S LVV Auger spectra from SF₆ excited by 196.5-eV photons and 3-keV electrons.

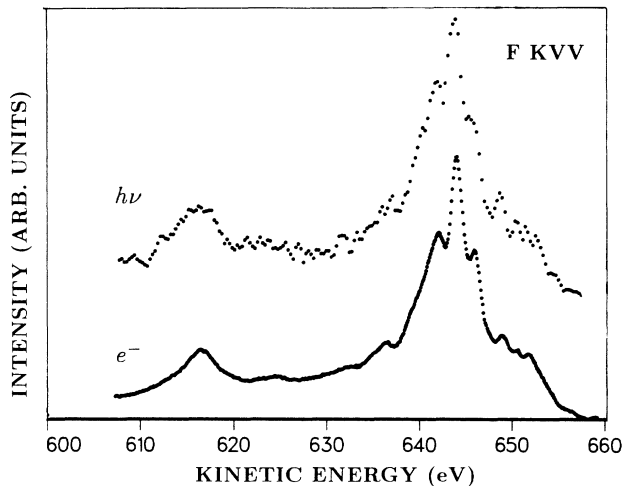


FIG. 3. Normal F *KVV* Auger spectra from SF₆ excited by 800-eV photons and 3-keV electrons.

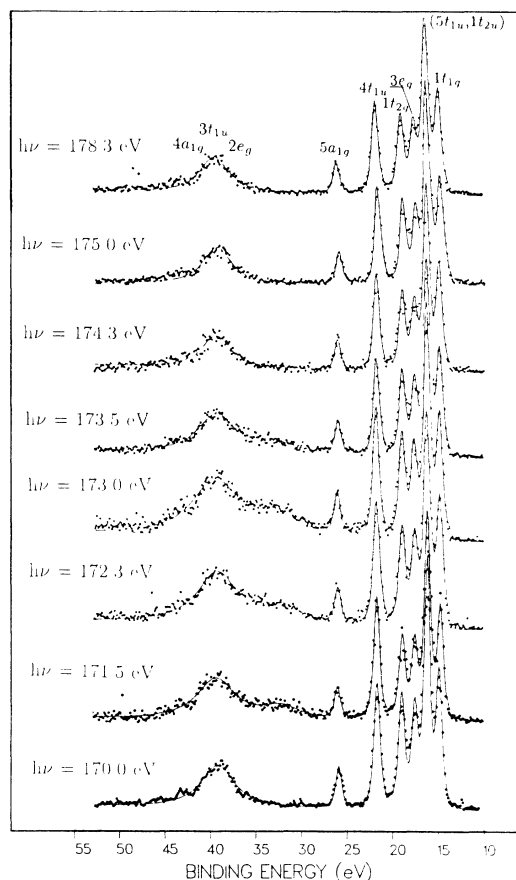


FIG. 4. Electron spectra of SF₆ in the binding-energy range 12–55 eV taken with indicated photon energies which cross the preedge resonances. Enhancement of the intensity in the range $E_B = 32$ –44 eV due to spectator resonance Auger phenomena is most obvious at the nominal photon energy of 173.0 eV. Solid curves represent least-squares fits to the experimental points.

should be calculated. Such calculations are possible, and very useful, for atoms,^{2,3,7,8} but not feasible for such a large molecule as SF₆ at the present time. Qualitatively, it is interesting to note that the energy separation between the two major peaks (~ 19 eV for S *LVV* and ~ 26 eV for F *LVV*) is different but roughly corresponds with the mean binding-energy difference (~ 21 eV) between the outer and inner valence-band peaks (Fig. 4 and Ref. 29). This clearly indicates that, depending on the initial core-hole atomic site (S or F), the joint valence orbitals of the final-state holes have different intensity contributions to the Auger spectrum. The transitions to the final-state orbitals which have the same character as the initial core-hole atom are favored in the Auger process. In the SF₆ molecule the outer most orbitals are mostly of F character. Also, the F *KVV* spectrum is qualitatively similar to the Ne *KLL* spectrum,^{8,29} although the widths of the F *KLL* spectrum are much broader, of course. Using the previous assignments for the Si *LVV* Auger spectra of SiF₄ and SiCl₄ as a guide,^{10,12,30} we can assign the low kinetic energy structures (at ~ 110 eV for S *LVV* and 617 eV for F *KVV*) to Auger transitions where one hole is in the outer valence band and the other hole is in the inner valence band. The high kinetic energy structure (at ~ 129 eV for S *LVV* and 643 eV for F *KVV*) can then be assigned mainly to Auger transitions where both final-state holes are in outer valence-band orbitals. As already mentioned, and also clearly indicated by the higher-resolution electron-excited spectra, these structures involve a very large number of line components.

B. Resonance Auger and participator decay at the S $2p \rightarrow 6a_{1g}$ and F $1s \rightarrow 6a_{1g}$ resonances

The intense preedge peak at 173 eV in the absorption spectrum (Fig. 1) corresponds to excitation of a S $2p$ electron to the $6a_{1g}$ antibonding orbital^{14,21} of high S $3s$ character.³¹ By recording high-resolution spectra between 15 and 55 eV binding energy (or ~ 160 - and ~ 120 -eV kinetic energy), we are able to observe the spectator and participator decay process. The spectra (Fig. 4) were taken with photon energies 170, 171.5, 172.3, 173, 173.5, 174.3, 175, and 178.3 eV—below, at, and above, the S $2p \rightarrow 6a_{1g}$ transition energy. The solid curves represent least-squares fits to the experimental spectra after subtraction of a linear background. The outer valence band ($E_B = 14$ –30 eV) has been fitted with six peaks^{20,29} due to the $1t_{1g}$, $(5t_{1u}, 1t_{2u})$, $3e_g$, $1t_{2g}$, $4t_{1u}$, and $5a_{1g}$ orbitals in order of increasing binding energy. The inner valence region ($E_B = 30$ –50 eV) has been fitted with two broad peaks: one for the F $2s$ peaks (from the unresolved $2e_g$, $3t_{1u}$, and $4a_{1g}$ orbitals²⁹), and one for the higher kinetic energy resonance Auger peak. The photon energy of 170 eV is well below the S $2p \rightarrow 6a_{1g}$ resonance. The electron spectrum at 170 eV (bottom spectrum, Fig. 4) thus represents a clean photoelectron spectrum without any contribution from decay processes involving the S $2p$ core hole, and this spectrum is used as a reference spectrum for the other spectra. The 170-eV spectrum shows once again^{20,29} that there are no obvious outer valence shakeup peaks in the 26–38 eV binding-energy region, and no sub-

stantial structure due to inner-valence configuration interaction in the 35–55 eV binding-energy region.

The additional intensity in the inner-valence region ($E_B \sim 33$ eV) at the resonance photon energies around 173 eV is distinctly seen (Fig. 4). The peak at ~ 33 -eV binding energy (~ 140 -eV kinetic energy for 173-eV photons) is at a similar, but higher (11.0 eV), kinetic energy relative to the high-energy normal Auger peak (Fig. 2), and thus, this peak can be assigned immediately to the corresponding resonance Auger peak. Obviously from Fig. 2, the Auger peak(s) at ~ 128 -eV kinetic energy do not have a well-defined shape, but a single-peak fit to the high kinetic energy maximum gives the position of the maximum within 0.3 eV. The accuracy to locate the position of the high-energy resonance Auger peak from the spectra of Fig. 4 is lower due to low intensity and overlap with inner-valence-band lines. Thus, our estimate for the kinetic energy shift between the highest kinetic energy peak of the resonance Auger spectrum and the normal Auger peak is 11.0 ± 1.0 eV. The lower kinetic energy normal Auger peak at ~ 110 eV should also have its resonant counterpart but because of much lower intensity we did not look specifically at this weaker peak. Since there are no radical changes in the intensity of the normal pho-

toelectron peaks of outer valence band, and the resonance Auger peak is very broad, it is qualitatively apparent that the resonance Auger process dominates over the participator process including the outer valence-band electrons.

In order to look more quantitatively at the relative intensities of all peaks near the 173-eV resonance, "difference" spectra were obtained by subtracting the normalized 170-eV referenced spectrum from the higher-photon-energy spectra at 171.5, 172.3, 173.0, and 173.5 eV (Fig. 5). The difference spectra were obtained from the least-squares fitted curves of Fig. 4. The spectra were normalized for subtraction by referencing to the $1t_{2g}$ line. Because it has 100% F $2p$ character,²⁹ no enhancement would be expected for its intensity. It is experimentally better resolved than $1t_{1g}$ and $3e_g$ lines which also have pure F $2p$ character. Most striking in the difference spectra [Fig. 5(b)] is the strong enhancement of the two broad peaks with binding energies ~ 40 and ~ 33 eV. The 33-eV binding-energy component is the expected spectator resonance Auger peak, but also the intensity of the F $2s$ photoelectron peaks (the most intense of which is the $3t_{1u}$ peak) is enhanced. The total intensity of the 33- and 40-eV binding-energy peaks increases on resonance at 173

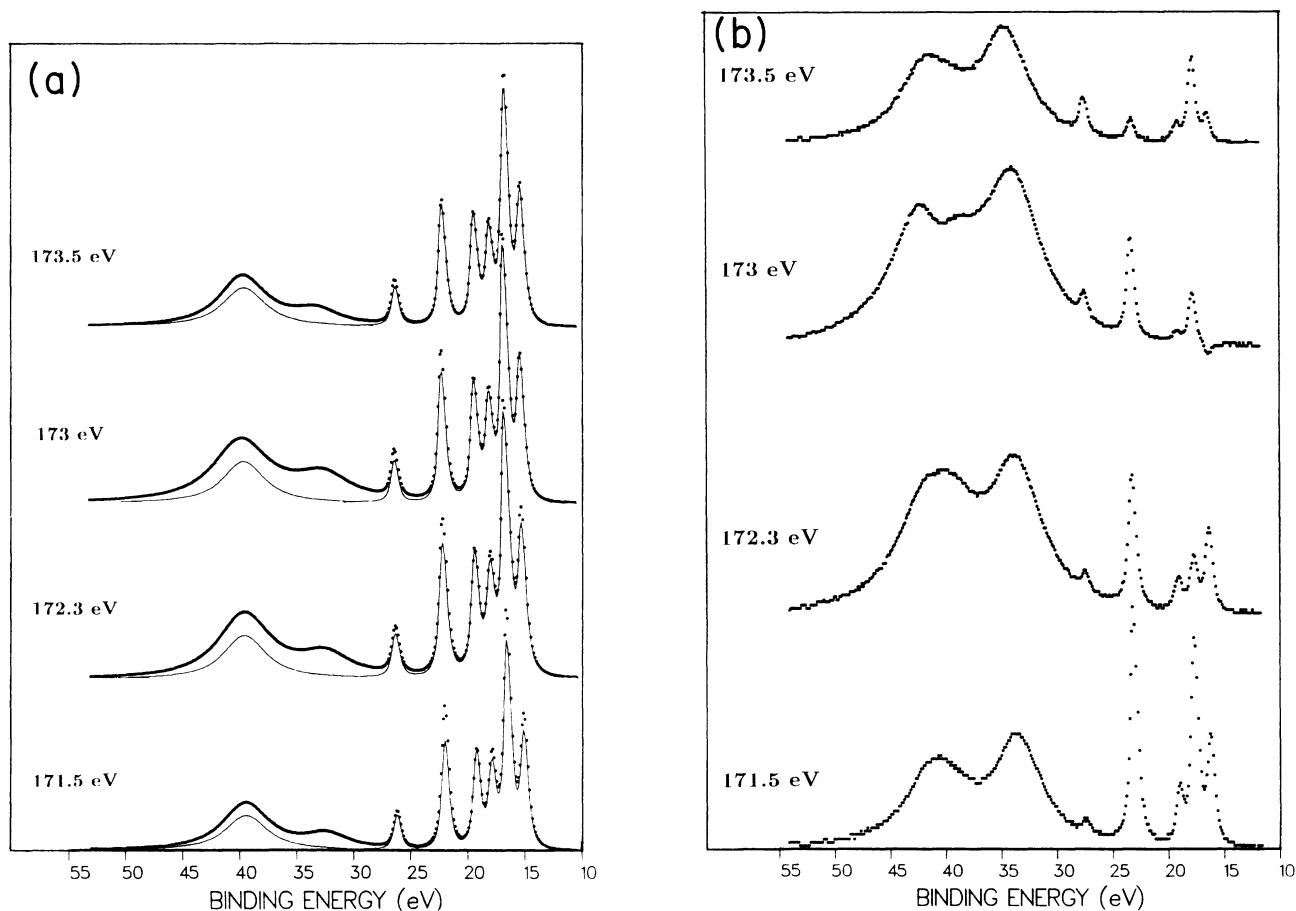


FIG. 5. (a) The least-squares-fitted curves of spectra taken at 171.5-, 172.3-, 173.0-, and 173.5-eV photon energies (points) compared with corresponding normalized fit curve of the reference spectrum taken at 170 eV (solid line). (b) The difference spectra between "resonance" spectra at 171.5-, 172.3-, 173.0-, and 173.5-, and 170-eV below-resonance reference spectrum.

eV to $\sim 60\%$ of the intensity of outer valence-band peaks. In contrast, the intensity of 33- and 40-eV peaks of resonance at 170 and 175 eV is only 31% of the outer valence-band intensity. The estimates are in good agreement with the previous results of Ferret *et al.*,¹⁴ who did not resolve the individual peaks. In addition, there is a consistent very strong enhancement of the $4t_{1u}$ outer valence peak at ~ 23 -eV binding energy; and smaller, but consistent, enhancements of the $(5t_{1u}, 1t_{2u})$ and $5a_{1g}$ peaks at ~ 18 - and ~ 27 -eV binding energy, respectively. Inconsistent enhancement of some of the other peaks is probably due mostly to statistical errors in the spectra. The difference spectra show that significant resonance excitation takes place from 171.5 through 173.5 eV. This is not unreasonable considering that the width (FWHM) of resonance absorption (Fig. 1) is ~ 2 eV, mainly due to the S $2p$ spin-orbit splitting of 1.2 eV. The origin of the enhancement of the ~ 40 -eV binding-energy F $2s$ peak in the difference spectra is not entirely clear. Most probably it is mainly caused by the participating F $2s$ process. A second possibility is that the ~ 40 -eV binding-energy peak is caused, to some extent, by the shakeup of the excited electron during the resonance Auger decay. This is analogous with the observed anomalously strong shakeup process in the case of the corresponding resonance Auger decay in atomic argon.⁷ The energy difference (~ 6 – 7 eV) between the two peaks in the difference spectra around the F $2s$ corresponds very well to the energy separation between $6a_{1g}$ and $6t_{1u}$ orbitals observed in x-ray-absorption spectra and our electron-energy-loss results, but is too small for $6a_{1g} \rightarrow 2t_{2g}$ shakeup which should be favored by g/u selection rules. Clear indications for similar resonance enhancement of F $2s$ intensity (the peak at 40 eV) is also seen in our previous SiF₄ results (Fig. 2 of Ref. 10). Thus, at the resonance photon energy of 106.5 eV, the F $2s$ peak is much more intense than at the off-resonance photon energy of 100 eV.

The F $1s$ absorption²⁵ and electron-energy-loss²⁴ spectra show, below the F $1s$ threshold, two prominent resonances corresponding to excitations to the $6a_{1g}$ and $6t_{1u}$ orbitals. We wanted to obtain similar electron spectra, to those obtained above (Fig. 4), at photon energies at the F $1s \rightarrow 6a_{1g}$ transition at 688 eV.²⁴ To obtain sufficient intensity with our monochromator at these high photon energies, we recorded spectra with slit widths of 70 μm which yielded photon widths of ~ 13 eV. The photon width is not small enough, of course, to record resolved valence-band spectra, to resolve excitations to the $6a_{1g}$ and $6t_{1u}$ orbitals, or to obtain distinct resonance Auger spectra. In order to enhance the resonance Auger spectrum with the $6a_{1g}$ electron as spectator, we set the mean photon energy at 680 eV and recorded spectrum in Fig. 6. This spectrum can be fitted reasonably by two peaks at 646- and 652-eV kinetic energies. Due to the high-energy tail of the broad photon width in addition to the $6a_{1g}$ also $6t_{1u}$ resonance excitation takes place as well as the ionization of the F $1s$ electrons [$E_B = 694.6$ eV (Ref. 29)]. Thus, the spectrum shown in Fig. 6 principally involves three different spectra corresponding to the two resonance excitations and the ionization. Because the $6t_{1u}$

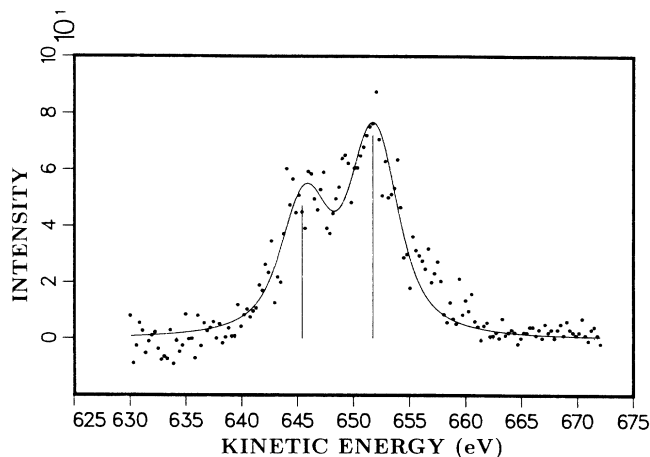


FIG. 6. Normal and resonance F KVV Auger spectra from SF₆ excited by the mean photon energy of 680 eV. The high-energy tail of broad photon bandwidth also caused $1s$ ionizations creating the normal Auger spectrum appearing in the spectrum as the lower kinetic energy peak of the doublet.

resonance is very close to the threshold the created resonance Auger spectrum is also energetically very close to and overlapping with the normal Auger spectrum. From Fig. 6, the shift between the high-energy resonance Auger peak corresponding excitations to the $6a_{1g}$ resonance and the combined $6t_{1u}$ resonance and normal Auger peak is 6.0 ± 0.5 eV. Principally, post-collision interaction for photon energies near threshold F $1s$ photoionization could also contribute to the shape and position of the lower kinetic energy peak. These effects are, however, expected to be very small compared, e.g., with the molecular line broadening. Comparison with the normal Auger spectrum (Fig. 3) shows that the low kinetic energy peak of Fig. 6 has about 2 eV higher kinetic energy. Thus, the shift between $6a_{1g}$ resonance Auger and normal Auger spectrum is 8.0 ± 1.0 eV. These resonance Auger shifts are determined by applying a simplified analysis but should be qualitatively correct.

The different resonance Auger shifts for the S LVV and F KVV spectra (11.0 and 8.0 eV, respectively) are interesting because these are among the first shifts measured on two different atoms in a molecule with the spectator electron in the same orbital. The larger shift for the S LVV resonance Auger spectrum is perhaps initially surprising; but these shifts are readily rationalized after looking at the positions of the $6a_{1g}$ resonances in the F $1s$ and S $2p$ electron energy-loss and absorption spectrum,^{24,25} Hitchcock's discussion, and the causes of Auger chemical shifts. The S $2p \rightarrow 6a_{1g}$ resonance is 8.4 eV below the S $2p$ ionization threshold, whereas the F $1s \rightarrow 6a_{1g}$ resonance is only 6.6 eV below the F $1s$ ionization threshold. This perhaps surprising difference is qualitatively rationalized²⁴ in terms of the coupling of the core analogy treatment with the double-well, potential barrier model.²⁴ The $6a_{1g}$ inner-well orbital is localized around the sulfur atoms, and the promotion of a sulfur

core electron to the $6a_{1g}$ orbital increases the effective core potential felt by this orbital much more than the increase due to the core charge on the ligand F atoms in the $F 1s \rightarrow 6a_{1g}$ excitation.

The different S LVV and F KVV Auger chemical shifts are probably not surprising now after looking at the approximate equation for the Auger chemical shift, ΔE_{Aug} .³²

$$\Delta E_{\text{Aug}} = -\Delta V + 3\Delta R, \quad (1)$$

where ΔV is the Madelung potential contribution to the core chemical shift due to the spectator $6a_{1g}$ electron and $3\Delta R$ is the change in total relaxation due to the creation of the core-hole and the double-hole final state. The Madelung ΔV term is normally much larger than the relaxation terms.^{32,33} Since the $6a_{1g}$ electron with the S $2p$ core hole is more tightly held (has a larger $\langle 1/r \rangle$ value) than with the F $1s$ core hole, the ΔV contribution to the S LVV Auger shift will be substantially larger than for the F KVV Auger shift, as observed. Indeed, the ΔV contribution to the x-ray photoemission spectroscopy (XPS) and resonance Auger chemical shifts is almost linearly related to the binding energy of the valence electrons³⁴ and Rydberg electrons,^{2,3} respectively.

The above ΔV contribution can also be used to rationalize the relative Auger chemical shifts in SF_6 and SiF_4 where the spectator σ^* electron in both cases has a very high-S or Si $3s$ character. In SiF_4 , the spectator electron is bound by 5.6 eV and yields an Auger chemical shift of 7.5 eV;¹⁰ in SF_6 , the spectator electron is bound by 8.6 eV and gives an Auger chemical shift of 11.0 eV. Again there is close to a linear relationship between the binding energy and the chemical shift. This relationship does not hold for spectator electrons in orbitals for which the $3s$ character is smaller—for example, in SiCl_4 where the more delocalized σ^* orbital is bound by 5.9 eV and leads to an Auger chemical shift of only 5.2 eV.¹²

Figure 7 examines, in more detail, the relative valence-

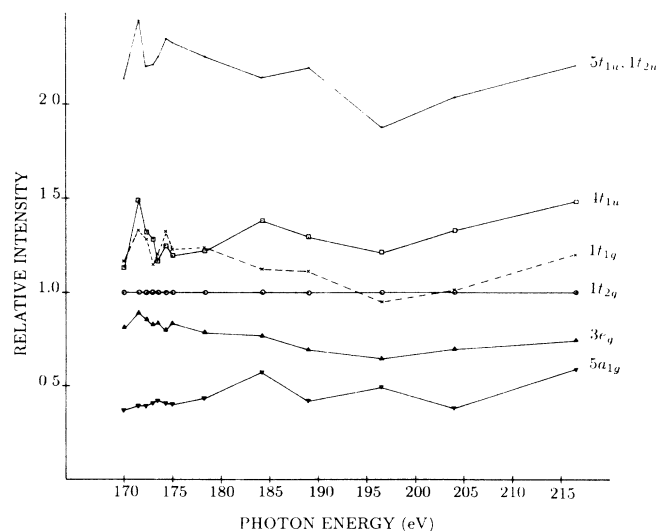


FIG. 7. Relative intensities of outer valence-band line components as the function of photon energy around S $2p$ resonance excitations.

band intensities both around the S $2p \rightarrow 6a_{1g}$ resonance and at higher energies corresponding to the above-edge resonances in Fig. 1. This figure shows once again that the $4t_{1u}$ and (5_{1u} , $1t_{2u}$ peaks) are enhanced at the $6a_{1g}$ resonance [see also Fig. 5(b)]. The $4t_{1u}$ and the $4a_{1g}$ and $3t_{1u}$ orbitals [which are also enhanced at the resonance, Fig. 5(b)] are binding orbitals with the highest sulfur character—19% S $3p$ for $4t_{1u}$, 20% S $3p$ for $3t_{1u}$, and 33% S $2s$ for $4a_{1g}$,²⁹ while the $5t_{1u}$ and $5a_{1g}$ orbitals are the only other orbitals having significant S character.²⁹ As discussed by Carlson *et al.*¹³ for the bonding $7t_2$ valence orbital for SiCl_4 which is enhanced at the Si $2p$ - σ^* preedge resonance, decay to a vacancy in an orbital of high-S character would be favored relative to fluorine lone pair orbitals. The enhancement of the $4t_{1u}$, $4a_{1g}$, $3t_{1u}$, $5t_{1u}$, $1t_{2u}$, and $5a_{1g}$ peaks is thus not surprising, and shows that significant participator decay to a central atom core hole will normally only involve bonding orbitals with significant central atom character. With more electropositive ligands such as CH_3 or H, the participator process should be more important as seen by de Souza *et al.*³⁵ in SiH_4 .

C. The valence electron spectra above threshold

As pointed out in the Introduction, Ferrett *et al.*¹⁴ noted the existence of a shakeup state or many-electron state which makes a significant contribution to the e_g shape resonance (no. 2 in Fig. 1) at 196 eV. If such SF_6 shakeup states above threshold should yield different Auger and/or valence-band spectra, was studied next. Figure 8 shows valence-band and Auger spectra at resonances 2, 3, and 4 of Fig. 1 (at 196.5, 206.5, and 216.5 eV), respectively, taken at medium resolution. The large increase in Auger intensity at 196.5 eV is obvious, and this intensity as noted by Ferret *et al.*¹⁴ (Fig. 4, no. 14) follows the S $2p$ cross section closely. There are no substantial changes in the broad Auger profiles over these energies, however. It

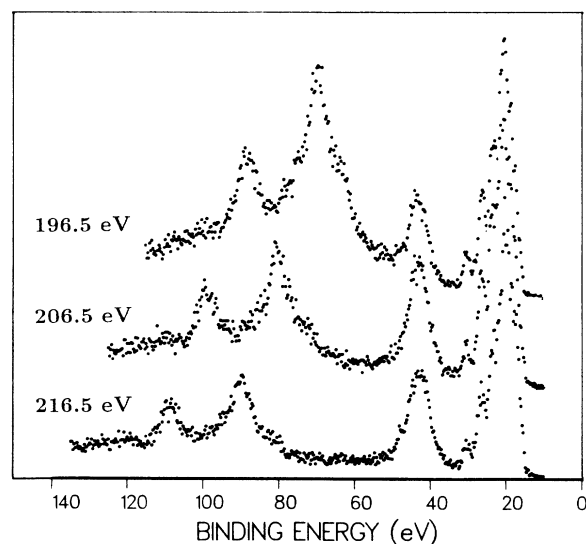


FIG. 8. The electron spectra above the S $2p$ edge at the resonance positions 2, 3, and 4 in Fig. 1.

would be rather difficult to see any new ion states in Fig. 8 even if they were there. Also, the valence-band intensities from the high-resolution spectra do not vary greatly at these resonances (Fig. 7), although the F 2s intensities do apparently increase relatively (Fig. 8) at resonance energies 206.5 and 216.5 eV compared to 196.5 eV. The result is not in conflict with the ideas proposed by Ferrett *et al.*¹⁴ but only shows that many-electron states seem not to cause any significant changes in the valence-band photoelectron and Auger spectra.

IV. CONCLUSIONS

Resonance Auger spectra of SF₆ following excitation of S 2p and F 1s electrons to the resonance orbitals have been studied with high-electron-energy resolution. The kinetic energy shifts of the resonance Auger spectra due to the spectator 6a_{1g} electrons have found to be 11.0 and 8.0 eV for S LVV and F KVV transitions and in comparison to the corresponding shift 7.5 eV of Si LVV in SiF₄. The spectator decay process has been found to be dominating decay channel but clear resonance behavior has

been observed for autoionization especially to 4t_{1u}, (3t_{1u}, 4a_{2g}), and (5t_{1u}, 1t_{2u}) orbitals.³⁶ An interesting doublet structure of the resonance Auger peaks around 173-eV photon energies has been found which could be caused by strong enhancement of the F 2s autoionization decay channel combined with the shakeup process during the Auger decay. The valence-band photoelectron and Auger spectra taken at shape resonances above the S 2p ionization do not show any significant changes.

ACKNOWLEDGMENTS

We would like to acknowledge the financial support from the National Research Council of Canada (NRC), the Natural Sciences and Engineering Research Council of Canada (NSERC), the University of Western Ontario, and the Finnish Academy of Science. We would also like to acknowledge the Synchrotron Radiation Center staff for their helpful assistance and Dr. J. S. Tse and Dr. N. Kosugi for communicating their results prior to publication.

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