Partial photoionization cross sections of SF$_6$ between 20 and 54 eV: An interpretation of the photoelectron spectrum

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The partial photoionization cross sections of sulphur hexafluoride have been measured between 20 and 54 eV using synchrotron radiation. Some of these cross sections are dominated by strong resonance effects. These resonances are shape resonances, resulting from the interaction between the photoelectron and the molecular field and hence always occur at approximately the same photoelectron kinetic energy. Expressed somewhat differently, they are final-state effects and can be thought of as arising from the multiple scattering of the photoelectron. Following Dehmer, the prominent resonance immediately above threshold in SF$_6$ is identified as having g symmetry. Hence, only valence orbitals with u symmetry may couple to it. This provides a powerful selection rule, which allows making an assignment of the peaks in the photoelectron spectrum. Even in the absence of resonances, the partial cross sections are qualitatively different for different orbitals. It is argued that measurements and calculations of partial cross sections should, in many cases, yield easier and more unambiguous assignments of peaks in photoelectron spectra than corresponding studies of ionization potentials.

I. INTRODUCTION

The advent of a synchrotron radiation as an intense source of light may be expected to have a major impact on the field of molecular photoelectron spectroscopy. While a wealth of valuable information can be obtained by measuring ionization potentials (electron-binding energies), it is now possible to proceed one step further and in detail map out the frequency dependence of the partial photoionization cross sections. Such measurements are important by themselves in that they will undoubtedly provide a better understanding of the basic physics of the photoionization process.[1] Another area where such data have already been shown to be of fundamental significance is surface physics: an understanding of the photoelectric properties of an adsorbed molecule requires a detailed understanding of the same properties of the free molecule.[2]

The purpose of the present paper is to illustrate, for what I believe to be the first time, a third utilization of such data: The assignment of the peaks in photoelectron spectra to molecular orbitals is usually made by comparing the measured spectra with computed ionization potentials. Unfortunately in many cases the energy separation between two ionization potentials is of the same order as the accuracy of the calculations. However, the symmetry properties of two such states may be very different. What I would like to point out is that these differences in symmetry may manifest themselves in the frequency dependence of the partial cross sections. These manifestations

may be so clear that an assignment of the various ionization potentials in terms of electronic states may be attempted. The specific case that will be studied here is SF$_6$.

The electronic excitations in SF$_6$ have been the subject of considerable study for some time.[3] The experimental techniques employed include x-ray absorption and emission,[4-9] optical absorp-
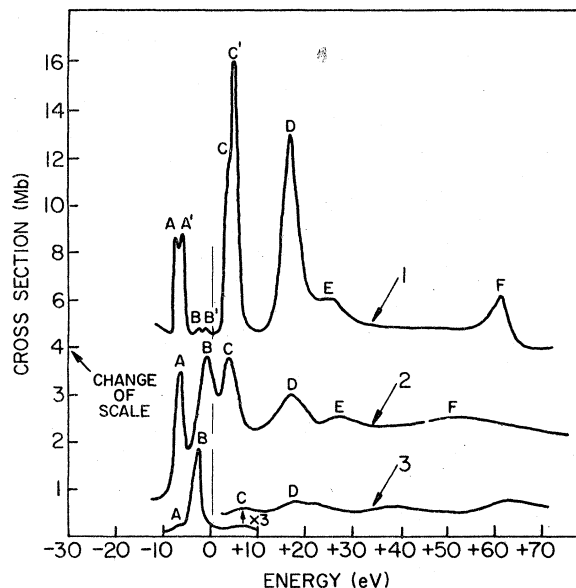

FIG. 1. X-ray absorption spectra of SF$_6$. Curve 1 is the sulphur $L_{\mathrm{II,III}}$ spectrum, curve 2 the fluorine K spectrum, and curve 3 the sulphur K spectrum. The figure is from Ref. 21.

tion[8, 10-13] photoelectron (uv[14, 15] and x-ray[16, 17] induced) emission, electron-energy-loss spectroscopy,[18] and photodissociation.[19] The main reason for all this activity is the complex structure of the x-ray spectra. Figure 1 shows some examples of the x-ray absorption spectra of SF_6. These spectra are remarkable in that they show strong absorption *bands*, whereas most atomic spectra show sharp Rydberg series and a more or less structureless continuum.

The outline of this paper is as follows: Section II contains a discussion of some theoretical concepts, in particular, effective potential barriers,[20-22] which are of fundamental importance for this work. Section III describes briefly the experimental procedure. The results are presented in Sec. IV. My interpretation of the photoelectron spectrum of SF_6 is given in Sec. V as well as a discussion of previous assignments. Section VI finally, summarizes my findings and points out some implications.

II. THEORETICAL BACKGROUND

The x-ray absorption spectra of atoms usually show sharp line structure due to Rydberg series below the ionization thresholds, followed by a rather structureless continuum. The x-ray spectra of a class of molecules which includes SF_6, differ in several notable respects from this behavior.[21] The Rydberg series in these molecules are quite weak.[9-11, 13] Their x-ray absorption spectra are instead dominated by strong, 1-5 eV broad bands, located both below and above the ionization thresholds[4-9] (see also Fig. 1). The initial state in the photoabsorption event from these core levels cannot be changed greatly from atom to molecule. Instead, the change must be attributed to the fact that the molecular potential of the final state is very different from the atomic potential of the constituents. These specific molecular effects can be understood through the concept of effective potential barriers,[3, 20-22] as developed especially by Dehmer and co-workers.[21,22]

These authors have focused on two aspects of molecular potentials which cause them to behave quite differently from atomic potentials: anisotropy and physical size. The first of these can couple a photoelectron (even one formed initially as a p wave in K-shell excitation) to high-l partial waves, whereas in the atomic case the range of l's is limited to $l_0 \pm 1$. The second causes high-l partial waves, e.g., $l = 2, 3$ in N_2,[22, 23] to behave resonantly at modest photoelectron kinetic energies, whereas this would not happen in the corresponding separated or united atom limit. The theoretical signature of such resonances is that

one of the scattering phase shifts of the molecular potential will vary rapidly as a function of energy through the resonant energy. An example of a thoroughly studied resonance is the resonance with σ_u symmetry at ~0.8 Ry kinetic energy in N_2. This resonance has been observed both in "*pseudo-x-ray*"[25] and uv absorption,[24, 26] both in N_2 and in the isoelectronic molecule CO. It has been shown both experimentally[27] and theoretically[22, 23] that this resonance can only be excited with an A-vector component parallel to the molecular axis. These resonances can of course be classified as to symmetry in the same manner as the occupied states. In particular for molecules with an inversion center, they possess u or g symmetry. Hence some, but not all, initial states can couple to them.[21, 23, 24] This provides a powerful selection rule, which as will be seen below, forms the basis for my interpretation of the valence photoelectron spectrum of SF_6.

The geometrical arrangement of the ligands around the central sulphur atom in SF_6 provides extremely favorable conditions for the existence of resonances. The large number of these resonances is immediately obvious from Fig. 1.[21] The spectra in Fig. 1 have been aligned in such a way that the zero of energy corresponds to the ionization threshold. This manner of displaying data is convenient when identifying final-state (kinetic energy) effects, and parallels the use of constant-ionic-state (CIS) spectra to be discussed in Sec. IV. As pointed out by Dehmer,[21] curve 1 (sulphur $L_{II,III}$ spectrum) will only show final-state resonances of g symmetry (the initial state is $2t_{1u}$). Similarly, curve 3 (sulphur K spectrum, initial state $1a_{1g}$) will only show resonances of u symmetry. Curve 2 (fluorine K, initial states $2a_{1g}$, $1t_{1u}$, $1e_g$) shows both types of final states. From Fig. 1 we can then conclude that a resonance with g symmetry exists a few eV above the ionization threshold. Dehmer has identified this state as corresponding to the molecular $2t_{2g}$ orbital.[21] Likewise, there is a shallow unoccupied orbital of u symmetry ($6t_{1u}$) below threshold (see curve 3), as well as a deeper g state ($6a_{1g}$) (see curve 1). This qualitative discussion of the $2t_{2g}$ state has been put on a quantitative footing by an MS-SCF $X\alpha$ (multiple-scattering—self-consistent-field $X\alpha$) calculation by Sachenko et al.[28] It should be stressed that the sulphur K spectrum in SF_6 (curve 3, Fig. 1) is quite different from the same spectrum in H_2S,[4, 29] indicating as anticipated above, the importance of the molecular potential for these spectra. I will show below how some of these resonances manifest themselves in the energy dependence for photoexcitation from the valence orbitals of SF_6.

The uv-photoelectron spectrum of SF$_6$ shows six well separated bands in the valence region.[14, 15] From group theory and elementary chemical arguments, it can be shown that there exist seven different valence levels. One of the peaks in the photoelectron spectrum has to be a doublet. Potts *et al.* observed the splitting of one of these six peaks *both* in the 21.2-eV photoelectron spectrum *and* in the 40.8-eV spectrum, and assigned two orbitals to this peak.[14] While it appears to be well established that this peak is split in the 21.2-eV spectrum, later work by Karlsson *et al.* did not confirm the existence of a splitting in the 40.8-eV spectrum.[15] Karlsson *et al.* concluded that in their investigation it was not possible to unambiguously assign one of the bands to ionization of two different orbitals.[15] To resolve this question it would obviously be desirable to have data at more photon energies. I will show below how the continuum nature of synchrotron radiation can be used also to elucidate the origin of the splitting in the 21.2-eV spectrum.

The ESCA (electron spectroscopy for chemical analysis) spectrum of the valence levels of SF$_6$ was first reported by Siegbahn *et al.*[16] Their tentative assignment of the bands, based on a complete neglect of differential overlap (CNDO) calculation, differs from the assignment given by Potts *et al.*[14] Another still different assignment has later been proposed by Gelius.[17] Using monochromatized x-ray radiation and intensity arguments, he obtained an ordering of the level which was identical with the result of a MS-SCF $X\alpha$ calculation by Connolly and Johnson.[30] LaVilla has, based on the photoelectron spectra and x-ray emission and absorption spectra, proposed still another assignment of the valence levels.[7]

The ordering of the valence levels of SF$_6$ has been the subject of several different theoretical studies.[16, 30-36] The methods used include Hartree-Fock,[31, 33, 34] CNDO,[16, 32] and MS $X\alpha$.[30, 35] In addition, von Niessen *et al.*[36] have reported a sophisticated calculation, based on, in most cases, an extremely successful Green's-function approach. Starting from Hartree-Fock they have by a perturbative approach, included corrections to the energy eigenvalues due to correlation effects.[36] All the reported calculations[16, 30-36] place the a_{1g}, t_{1u}, and the first t_{2g} level in a group with higher-binding energies than another group with the t_{2u}, e_g, t_{1g}, and another t_{1u} level.[16, 30, 36] However, there is little agreement between different calculations as to the detailed ordering within each group. In fact, of the six calculations reported prior to 1974,[16, 30-34] no two agreed on the ordering of all levels! The $X\alpha$ calculation by Rösch *et al.*[35] used almost the same input parameters as Con-

nolly and Johnson[30] and obtained, not unexpectedly, almost identical results. This was also the order found by von Niessen *et al.*[36]

Their is no doubt which orbitals are occupied, only their relative ordering is uncertain. The configuration obtained by von Niessen *et al.* in order of decreasing binding energy and including core orbitals[36] is

$$(1a_{1g})^2 (2a_{1g})^2 (1e_g)^4 (1t_{1u})^6 (3a_{1g})^2 (2t_{1u})^6$$

$$(4a_{1g})^2 (2e_g)^4 (3t_{1u})^6 (5a_{1g})^2 (4t_{1u})^6 (1t_{2g})^6$$

$$(3e_g)^4 (1t_{2u})^6 (5t_{1u})^6 (1t_{1g})^6 .$$

The $1t_{2u}$ and $5t_{1u}$ orbitals are almost degenerate in this calculation. This was interpreted to mean that they formed overlapping bands in the uv-photoemission spectrum.[36] This calculation also suggests that many electron effects (shake-ups, etc.) are of little importance for the spectral function.

The uv-photoabsorption spectrum of SF$_6$ is quite complex. As in the case of the x-ray spectra, the Rydberg series are very weak.[8, 10-13] Also here, broad bands are observed. It has so far not been possible to correlate these bands with particular final states as has been done in the case of the x-ray spectra.[21] This is obviously due to the fact that the absorption spectra of several occupied levels overlap.

III. EXPERIMENTAL

The experimental setup built by Eastman and co-workers, is essentially the same as the one described earlier[24, 37] and will therefore only be discussed briefly here.

Synchrotron radiation from the 240-MeV electron storage ring at the Physical Sciences Laboratory at the University of Wisconsin is dispersed by a 1-m horizontally mounted Seya-Namioka monochromator. The wavelength resolution of the monochromator is externally variable in steps from 1.6 to 16 Å. The light from the monochromator is estimated to be 80% polarized in the horizontal plane. The light intensity was measured with a calibrated Al diode.

The gas was admitted to the interaction region through a nozzle with a hole of 1 mm diameter. It was found to be extremely important to align the nozzle with the energy analyzer and the light beam, in order to obtain optimum counting rates. The gas was continuously pumped out with a 200-liter/sec turbomolecular pump. This pump contributed a significantly smaller background of

low-energy electrons that the ion pump used earlier.[24]

The electron-energy analyzer is a two-stage cylindrical mirror analyzer PHI model No. 250. This analyzer has the great advantage that it has well-understood transmission properties as well as a high angular acceptance. The pass energy of the analyzer was higher than 30 eV in order to avoid distortion of the energy distribution.[24] The spatial arrangement of the analyzer relative to the light beam introduces, as discussed earlier, a geometry-dependent systematic error in our measurements. That is, if the real cross section is σ_0 and the angular symmetry parameter is β, we measure a cross section σ_m

$$\sigma_m \approx \sigma_0 (1 - 0.16\beta) . \tag{1}$$

In the cases investigated earlier, namely, N_2 and CO, we found that this error was not important.[24]

The pressure in the interaction region was estimated to be between 10^{-3} and 10^{-4} torr.[24] The upper limit is set by the vacuum requirements of the channel electron multiplier which serves as detector in the energy analyzer.

The data were collected in a multichannel analyzer using multiple sweeps in order to eliminate effects of changes in light intensity and gas pressure. The measured light intensity from the monochromator in these experiments is given in Fig. 12, of Ref. 24 (the higher amplitude curve).

The counting rates depend among other things, on the photoionization cross sections and the photon flux from the monochromator. Under favorable conditions the accumulation time for a spectrum with $\hbar\omega \geq 50$ eV at total energy resolution of 0.5 eV was 15–20 min. At lower photon energies both the cross section and the photon flux increase substantially and an energy distribution could be recorded in less than a minute.

The measurements reported here are of two kinds, EDC's and CIS's.[24] The electron-kinetic-energy distributions (EDC's) are obtained at fixed photon energies. The area under the various peaks in these curves (each peak corresponds to a different state of the ion after photoexcitation) is measured (see Fig. 2). From these areas the branching ratio can be calculated. The CIS[24, 39] spectra for each peak are measured by synchronously sweeping the photon energy passed by the monochromator and the electron kinetic energy being passed by the electron-energy analyzer. These spectra were measured with a calibrated Al diode as monitor of the light intensity. The light from the monochromator hits the diode after interacting with the gas. Both the EDC's and the
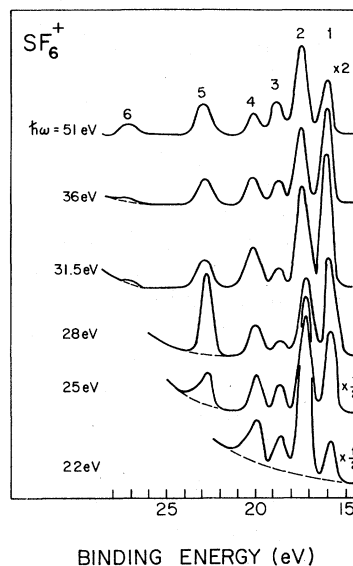

FIG. 2. Examples of energy distribution curves for SF_6. The curves are normalized relative to each other using the photoabsorption data from Ref. 12. The dotted curve denotes the background.

CIS's are distorted at low kinetic energies by a smooth background, arising primarily from light hitting the magnetic shield around the energy analyzer. This background is easy to separate out in the EDC's (shown as dashed lines in Fig. 2), but makes it difficult to directly convert to CIS's into absolute cross sections at present. We will, therefore, only attribute significance to *structure* in the CIS's.

Electron-kinetic-energy distributions were obtained every 0.5 eV from the ionization threshold to 40 eV and from there every eV to 54 eV. These spectra were obtained with moderate resolution, as discussed above. Additional spectra with higher resolution were obtained between 20 and 25 eV to study the anomalous splitting of one peak in the $\hbar\omega = 21.2$-eV spectrum. The constant-ionic-state spectra were obtained for the five outermost bands in the photoexcitation spectrum between threshold and $\hbar\omega = 40$ eV.

As the two published $\hbar\omega = 40.8$ eV (He II) spectra differ significantly,[14, 15] it was considered worthwhile to repeat these measurements. The experimental equipment for these studies consisted of a commercial Vacuum Generators UVG3 photoelectron spectrometer. This spectrometer, which is intended for high-precision measurements of ionization potentials and not branching ratios, has a collection efficiency with a large β dependence.

Hence, I will not attribute significance to the branching ratios that could be derived from the data obtained with this instrument.

IV. RESULTS

Some representative EDC's are shown in Fig. 2. The peaks in the EDC's are numbered 1–6 in increasing binding energy. It is very striking how the relative amplitude of these peaks changes with photon energy. For example, at $\hbar\omega = 22$ eV, peak 2 is the largest, at $\hbar\omega = 36$ eV, peak 1 is strongest and at $\hbar\omega = 51$ eV, peak 2 is again the largest. Peak 5 changes its relative magnitude very drastically near $\hbar\omega = 28$ eV.

The results of my studies with He I and II radiation are shown in Fig. 3, curves a and b. The data agree with those of Karlsson et al.[15] and differ from those of Potts et al.[14] in that peak number 3 is found to be split at $\hbar\omega = 21.2$ eV but *not* at $\hbar\omega = 40.8$ eV. Also shown in Fig. 3 (curves $c-e$) are synchrotron radiation data, which show convincingly that the behavior of peak 3 is anomalous in a narrow interval around $\hbar\omega = 21.2$ eV. No such behavior is observed around $\hbar\omega = 40.8$ eV.

There exist differences in the amplitude ratio of the two components in peak 3 between the data in Figs. 3(b) and 3(d). This ratio varies quite rapidly with wavelength near $\hbar\omega = 21.2$ eV. As the data in Figs. 3(b) and 3(d) were taken with different wavelength resolution, it is not surprising that this ratio differs in the two spectra. There is also a
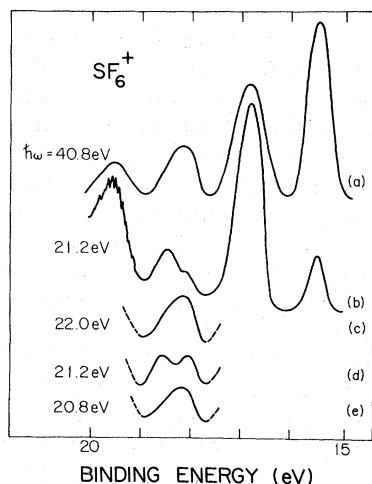

FIG. 4. β-dependent branching ratios for SF$_6$ for the five peaks in the EDC's with lowest-binding energies. Panels (a)–(e) correspond to peaks 1–5 (Fig. 2), respectively. They are also identified by their (vertical) ionization potentials.

difference in this ratio between our HeI data and those by Karsson et al.[15] One possible explanation is a different β dependence of the two analyzers [Eq. (1)].

Figure 4 shows the branching ratios obtained from curves like the ones in Fig. 2. The branching ratios obtained from peak 6 are small, ranging from less than a few percent around threshold up to around 5% at 50 eV. The scatter between points is not insignificant and the branching ratio does not show any structure. Hence, I do not show these data here.

The partial photoionization cross sections are shown in Fig. 5. (The cross section for peak 6 is

FIG. 3. Electron-kinetic-energy distributions obtained with He-resonance radiation (curves a and b). Also shown are portions of EDC's obtained by synchrotron radiation around 21 eV (curves $c-e$).
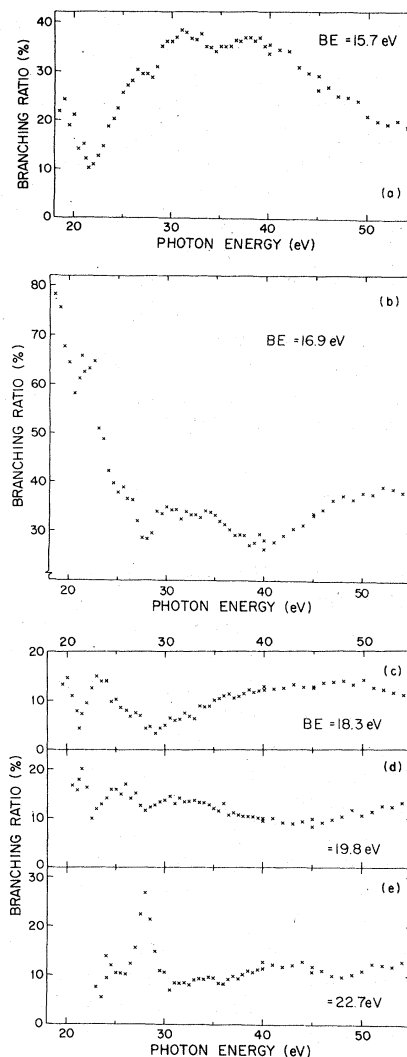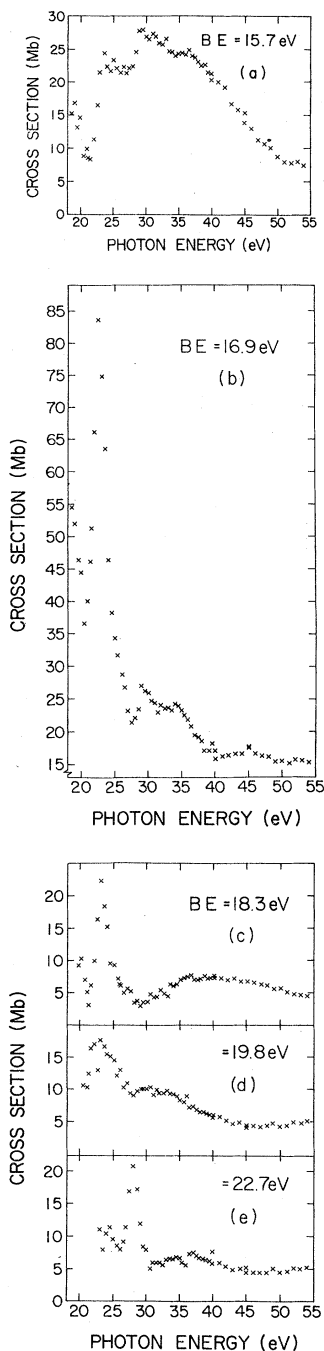
FIG. 5. Partial photoionization cross sections (Ref. 38) for SF$_6$ for the five peaks in the EDC's with lowest-binding energy. See the text for further details.

small. It increases slowly and almost monotonically from threshold, never exceeding 3 Mb. It is, therefore, not shown here.) The partial photoionization cross sections were obtained using the branching ratios in Fig. 4 and the recent photoabsorption data by Lee et al.[13] I have *assumed* the

photoionization efficiency (γ) of SF$_6$ to be 1 over the whole energy range. The only reported γ values for SF$_6$ are due to Sasanuma et al.[12] Their results are rather remarkable in that their maximum value of γ is 0.3. It is very difficult to understand what sort of physical mechanisms can give rise to such a low photoionization efficiency. It is difficult to assess from the published report how the photoionization efficiency was measured. It is, for example, well known that the SF$_6^+$ ion has a large probability for subsequent dissociation.[19] The effect of this dissociation on the photoionization efficiency measurements is not known. If we were to use the γ values of Sasanuma et al.,[12] the main effect would be to accentuate the cross sections around 20 eV. The structure in the curves would not change but the absolute values of the cross section clearly would.

I have made no attempt to study the fluorine 2s derived levels with binding energies around 40 eV ($3t_{1u}$, $2e_g$, and $4a_{1g}$). The branching ratios in Fig. 3 should hence be interpreted as giving the relative probability for photoexcitation *between the uppermost orbitals* only for $\hbar\omega$ greater than the threshold for photoionization from the fluorine 2s derived levels. The partial photoionization cross sections in Fig. 5 will be affected in a corresponding way.

As noted by Lee et al.[13] their total photoabsorption [$\sigma_{tot}(\omega)$] measurements are in good agreement with those of Sasanuma et al.[12] at low photon energies and with those of Blechschmidt et al.[8] at high photon energies. The data by Lee et al.[13] show considerably more detail than the earlier work.[8,12] The partial photoionization cross sections in Fig. 5 show somewhat more fine structure than do the branching ratios in Fig. 4. This fine structure occurs where $\sigma_{tot}(\omega)$ varies rapidly. I believe that this fine structure is spurious and caused by small differences in wavelength calibration between the monochromator used by Lee et al.[13] and the one used in the present work.

The partial photoionization cross sections in Fig. 5 are quite rich in structure. Particularly remarkable are the sharp peaks that appear in the spectra in panels (b), (c) and (e). It is also notable that almost the whole falloff of $\sigma_{tot}(\omega)$ above 40 eV is due to the band with the lowest binding energy [panel (a)].

At $\hbar\omega$ = 54 eV the relative strengths of the six bands are (in increasing binding energy and normalized to band 1) 1:2.1:0.6:0.7:0.7:0.3. This can be compared to the ESCA values (Al $K\alpha$, $\hbar\omega$ = 1486 eV) 1:1.9:0.8:0.7:2.4:2.6.[17]

Figure 6 shows CIS's for the five outermost peaks in Fig. 2 as a function of kinetic energy of the photoelectron. Observe in particular that
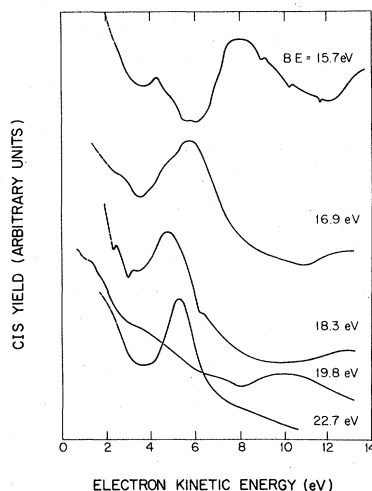
FIG. 6. Constant-ion-state spectra for the five outer-most peaks in the EDC as a function of kinetic energy. The spectra are not correctly scaled relative to each other.

three of the curves show a maximum between 5 and 6 eV kinetic energy. These three curves maxima correspond, after allowance is made for the differences in binding energy, to the three peaks in the partial photoionization cross sections in Fig. 5 panels (b), (c), and (e).

The autoionization decay from Rydberg states was studied in the CIS's much in the same way as done in earlier work on CO and N$_2$.[24] A few window-type resonances were observed [top curve in Fig. 6]. They were in essential agreement with earlier high-resolution optical absorption work.[8, 11, 13]

V. DISCUSSION

My interpretation of the photoelectron spectrum of SF$_6$ will rely on the identification of the final-state resonance a few eV above threshold as having g symmetry. The continuous nature of synchrotron radiation makes it possible to utilize this feature to identify the initial states of u symmetry. By choosing the appropriate photon energy it is possible to excite each level to a kinetic energy corresponding to this resonance. The only peaks that exhibit this resonance in the cross section correspond to u-type initial orbitals. One immediately sees (Figs. 5 and 6) that bands 2, 3, and 5 couple to this resonance whereas 1 and 4 do not. Of the three deepest-lying valence levels ($5a_{1g}$, $4t_{1u}$, and $1t_{2g}$, see Sec. II) only one has u symmetry. It follows that peak 5 should be identified with $4t_{1u}$.

The ESCA spectrum[16,17] of SF$_6$ is, as mentioned

above, dominated by peaks 5 and 6. One would then expect these orbitals to have appreciable s character. The $4t_{1u}$ orbital does indeed contain appreciable fluorine 2s contributions. This also implies that peak 6 has to be the only valence level with a significant sulfur 3s content, namely $5a_{1g}$. Peak 4 is then assigned to $1t_{2g}$. This is consistent with peaks 4 and 6 not coupling to the resonance.

The ordering of the three low-lying valence levels is then, in increasing binding energy: $1t_{2g}$, $4t_{1u}$, $5a_{1g}$. This is the same ordering as obtained by other means, for example, by Potts et al.[14] and by Gelius.[17]

From Figs. 5 and 6, one may make conclusions about the remaining valence levels also. As peaks 2 and 3 couple to the resonance they then have to each contain one of the two remaining u levels. Peak 1 does not go through this resonance and has to contain one g level. This differs from the earlier assignments.[14, 16, 17]

There remains two g levels and one unassigned band. One of the g levels has then to be associated with band 1. One now has to decide which band in the photoelectron spectrum is a doublet and thus contains the last g level.

From Fig. 3 one can see that the splitting of peak 3 only persists in a narrow photon energy range. Such perturbations of the shape of a band have been observed for example in O$_2$,[40] and have been attributed to autoionization. The same explanation is adopted here and will be discussed further below.

The cross section of peak 2 is larger than that of peaks 1 and 3, both in the uv range (Fig. 5) and in the ESCA spectrum.[16, 17] Although the Thomas-Reiche-Kuhn sum rule does not hold rigorously for individual orbitals, it seems nevertheless likely that peak 2 is the doublet. This has also been suggested by others.[17, 30, 35, 36] The present conclusion differs however, as to the composition of the doublet. I find that it has to consist of one u and one g orbital. Intensity arguments suggest that the g state is the fourfold-degenerate $3e_g$, rather than the sixfold-degenerate $1t_{1g}$. This is not unreasonable as the three calculations[30, 35, 36] that do agree as to the ordering of the valence levels place $1t_{1g}$ at a lower-binding energy than $3e_g$.

It appears not to be possible to assign the last two u levels, $5t_{1u}$ and $1t_{2u}$, based on intensity arguments without doing a calculation. The assignment that I arrive at is then, in increasing binding energy, $1t_{1g}$, ($5t_{1u}+3e_g$), $1t_{2u}$, $1t_{2g}$, $4t_{1u}$ and $5a_{1g}$, with $5t_{1u}$ and $1t_{2u}$ quite possibly reversed.

In light of these results, I will now proceed to make some comments on earlier spectroscopic data on SF$_6$.

As mentioned earlier, the Rydberg series in

SF$_6$ are very weak, the reason being that the potential barriers inhibit excitation to the diffuse Rydberg orbitals. Neverthelsss, a few weak series have been observed. Codling found a series nicely converging to 26.8 ± 0.04 eV, which corresponds to the binding energy of the $5a_{1g}$ orbital.[11] Nakamura et al. detected very weak structure around 180 eV which clearly is attributed to Rydberg series converging to the ionization limit of the $2t_{1u}$ state.[9] Potts et al. have attributed[14] some very weak structure first observed by Codling[11] to a Rydberg series converging to an ionization limit at 22.5 eV. A lower-energy member of the same series has recently been observed by Lee et al.[13] All these ionization limits are in good (± 0.05 eV) agreement with the photoelectron values for the binding energies. Nostrand and Duncan[10] observed four lines below the first ionization threshold. The first of these lines centered at $\hbar\omega = 11.5$ has a half width of some 2 eV, whereas the other three lines (at $\hbar\omega = 13.27$, $\hbar\omega = 14.28$, and $\hbar\omega = 15.16$ eV) are narrow. They fitted line numbers 1, 3, and 4 to a Rydberg series converging to $\hbar\omega = 16.15$ eV, which is 0.46 eV away from the nearest ionization potential. Subsequent measurements[8,18] have obtained essentially the same values for the first lines, but a significantly different value ($\hbar\omega = 14.9$ eV) for the highest one. I have tried to fit these new values to a Rydberg series, but without success. Indeed, I obtain even worse agreement than Nostrand and Duncan[10] for reasonable values of the quantum defect. There seems to be no alternative at present but to assume that lines 2–4 are members of one or possibly several deeply perturbed Rydberg series. The width of the peak around 11.7 eV is however, conspicuous. It is unlikely that the line shape can be attributed to interaction with the continuum,[41] as the adjacent continuum is quite weak.

It seems much more likely to assign this peak to transitions from an occupied valence orbital to an unoccupied one below the vacuum. Dehmer[21] obtained (see Fig. 1) a resonance with g (u) symmetry at 9.6 (3.3) eV below the vacuum. Since the binding energy of the $4t_{1u}$ orbital is 22.5 eV, for example, it would in single-particle terms, take 12.9 eV to take an electron from the $4t_{1u}$ orbital and put it in this resonance. From this single-particle estimate one should deduct the difference in screening energy of the hole between the valence-valence and core-valence excitations. If this is assumed to be of the order of 1 or 2 eV, the resulting transition could very well explain the broad peak in the adsorption spectrum just below 12 eV. Furthermore, there are two other symmetry-allowed transitions in this energy range, namely, from the $1t_{1g}$ and $3e_g$ orbitals to

the u resonance below the vacuum.

There will also be transitions from lower lying orbitals to these resonances below the vacuum. For example, without correction for differential hole screening, it would take 23.5 eV to move an electron from the $5a_{1g}$ orbital to the u resonance. Allowing a 2 eV reduction of this energy due to screening, the autoionization decay of this excitation could very well explain the asymmetric line shape of the third peak in the He I spectrum. As the $5t_{1u}$ and $1t_{2u}$ orbitals have very different spatial character,[33] it seems unlikely that they would couple equally strongly to these decay processes. It should be possible to separate them, e.g., by a calculation of the total energy curves.

The energy position of the g resonance in the continuum deserves mention. The peaks in Fig. 6 are located at 5.6 eV kinetic energy (excitations from band 2 in the photoelectron spectrum), 5.1 eV (band 3), and 5.7 eV kinetic energy (band 5). Using the x-ray data of Blechschmidt et al.[8] I obtain approximately 3.6 eV for the same quantity in the case of excitation from the sulphur 2p core level. The resonance in the core excitation thus appears at a slightly lower kinetic energy. This is the same trend as can be found both in N$_2$ and CO.[24] This may be due to differences in the initial-state wave functions or in the screening of the two hole states.

VI. CONCLUSIONS

Measurements of the partial photoionization cross sections of SF$_6$ between threshold and 54 eV photon energy have been reported. These cross sections are very rich in structure, showing dramatic resonance effects. A qualitative understanding of these effects can be obtained through the concept of effective potential barriers.[3,20-22] In this manner, the fundamental importance of the molecular potential for the outgoing photoelectron can be understood.

The existence of a final-state resonance of g symmetry between 5 and 6 eV kinetic energy has made an interpretation of the photoelectron spectrum of SF$_6$ possible. This identification is different from the one currently favored in the literature.[30,35,36]

In addition to the present results on SF$_6$, there now exists extensive partial photoionization cross-section data in the uv range on three more molecules, namely, CO,[24] N$_2$,[24] and CO$_2$.[42] In all cases, qualitative differences between the cross sections of different orbitals have been observed, even in the absence of resonances. It seems that even a fairly crude calculation should be able to explain these first-order effects. In order to perform or-

bital assignments, it may very well turn out to be advantageous to perform such calculations instead of further refining computations of energy eigenvalues. However, it is also quite clear that the potential that acts on the photoelectron is strong, i.e., the cross sections are very far from free-electron-like. Any calculation addressing itself to these problems must take this fundamental aspect of the problem into account.

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[1]J. A. R. Samson, Phys. Rep. 4, 303 (1976).

[2]T. Gustafsson and E. W. Plummer, in *Photoemission and the Electronic Structure of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, London, 1978).

[3]U. Fano, Comments At. Mol. Phys. 3, 75 (1972).

[4]R. E. LaVilla and R. D. Deslattes, J. Chem. Phys. 44, 3499 (1966).

[5]T. M. Zimkina and V. A. Formichev, Sov. Phys. Dokl. 11, 726 (1967).

[6]T. M. Zimkina and A. S. Vinogradov, J. Phys. (Paris) 32, C4-3 (1971).

[7]R. E. LaVilla, J. Chem. Phys. 57, 899 (1972).

[8]D. Blechschmidt, R. Haensel, E. E. Koch, U. Nielsen, and T. Sagawa, Chem. Phys. Lett. 14, 33 (1972).

[9]M. Nakamura, Y. Morioka, T. Hayaishi, E. Ishigura, and M. Sasanuma, Conference Digest, Third International Conference on Vacuum Ultraviolet Radiation Physics, Tokyo, Japan, 1971 (unpublished).

[10]E. D. Nostrand and A. B. F. Duncan, J. Am. Chem. Soc. 76, 3377 (1954).

[11]K. Codling, J. Chem. Phys. 44, 4401 (1966).

[12]M. Sasanuma, E. Ishiguro, Y. Morioka, and M. Nakamura, in Ref. 9.

[13]L. C. Lee, E. Phillips, and D. L. Judge, J. Chem. Phys. 67, 1237 (1977).

[14]A. W. Potts, H. J. Lempka, D. Y. Streets, and W. C. Price, Philos. Trans. R. Soc. Lond. A 268, 59 (1970).

[15]L. Karlson, L. Mattsson, R. Jadrny, T. Bergmark, and K. Siegbahn, Phys. Scr. 14, 230 (1976).

[16]K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hedén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969).

[17]U. Gelius, J. Electron. Spectrosc. 5, 985 (1974).

[18]J. A. Simpson, C. E. Kuyatt, and S. R. Mielczarek, J. Chem. Phys. 44, 4403 (1966).

[19]V. H. Dibeler and J. A. Walker, J. Chem. Phys. 44, 4405 (1966).

[20]V. I. Nefedov, J. Struct. Chem. 11, 277 (1970).

[21]J. L. Dehmer, J. Chem. Phys. 56, 4496 (1972).

[22]J. L. Dehmer and D. Dill, Phys. Rev. Lett. 35, 213 (1975); J. Chem. Phys. 65, 5327 (1976).

[23]J. W. Davenport, Phys. Rev. Lett. 36, 945 (1976).

[24]E. W. Plummer, T. Gustafsson, W. Gudat, and D. E. Eastman, Phys. Rev. A 15, 2339 (1977).

[25]G. R. Wight, C. E. Brion, and M. J. van der Wiel, J. Electron. Spectrosc. 1, 457 (1973).

[26]B. E. Cole and R. N. Dexter (private communication) have recently observed structure in the photoabsorption spectrum of CO and N$_2$ which they attribute to excitation from the 3σ and $2\sigma_g$ orbitals, respectively, to this resonance.

[27]C. L. Allyn, T. Gustafsson, and E. W. Plummer, Chem. Phys. Lett. 47, 127 (1977).

[28]V. P. Sachenko, E. V. Polozhenstev, A. P. Kovtun, Yu F. Migal, R. V. Vedrinski, and V. V. Kolesnikov, Phys. Lett. A 48, 169 (1974).

[29]G. Brogren, Ark. Mat. Astron. Fys. A 31, 23 (1945).

[30]J. W. D. Connolly and K. H. Johnson, Chem. Phys. Lett. 10, 616 (1971).

[31]G. L. Bendazolli, P. Palmieri, B. Cadioli, and U. Pincelli, Mol. Phys. 19, 865 (1970).

[32]D. P. Santry and G. A. Segal, J. Chem. Phys. 47, 158 (1967).

[33]F. A. Gianturco, C. Guidotti, U. Lamanna, and R. Moccia, Chem. Phys. Lett. 10, 269 (1971).

[34]B. Roos (unpublished), quoted in Ref. 30.

[35]N. Rösch, V. H. Smith, Jr., and M. H. Whangbo, J. Am. Chem. Soc. 96, 5984 (1974).

[36]W. von Niessen, L. S. Cederbaum, G. H. F. Diercksen, and G. Hohlneicher, Chem. Phys. 11, 399 (1975).

[37]D. E. Eastman, D. W. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B 9, 3472 (1974).

[38]The cross sections contain a β dependence given by Eq. (1).

[39]G. J. Lapeyre, J. Anderson, P. L. Gobby, and J. A. Knapp, Phys. Rev. Lett. 33, 1290 (1974).

[40]J. A. Kinsinger and J. W. Taylor, Int. J. Mass. Spectrom. Ion Phys. 11, 461 (1973).

[41]U. Fano, Phys. Rev. 124, 1866 (1961).

[42]T. Gustafsson, E. W. Plummer, D. E. Eastman, and W. Gudat, Phys. Rev. A 17, 175 (1978).