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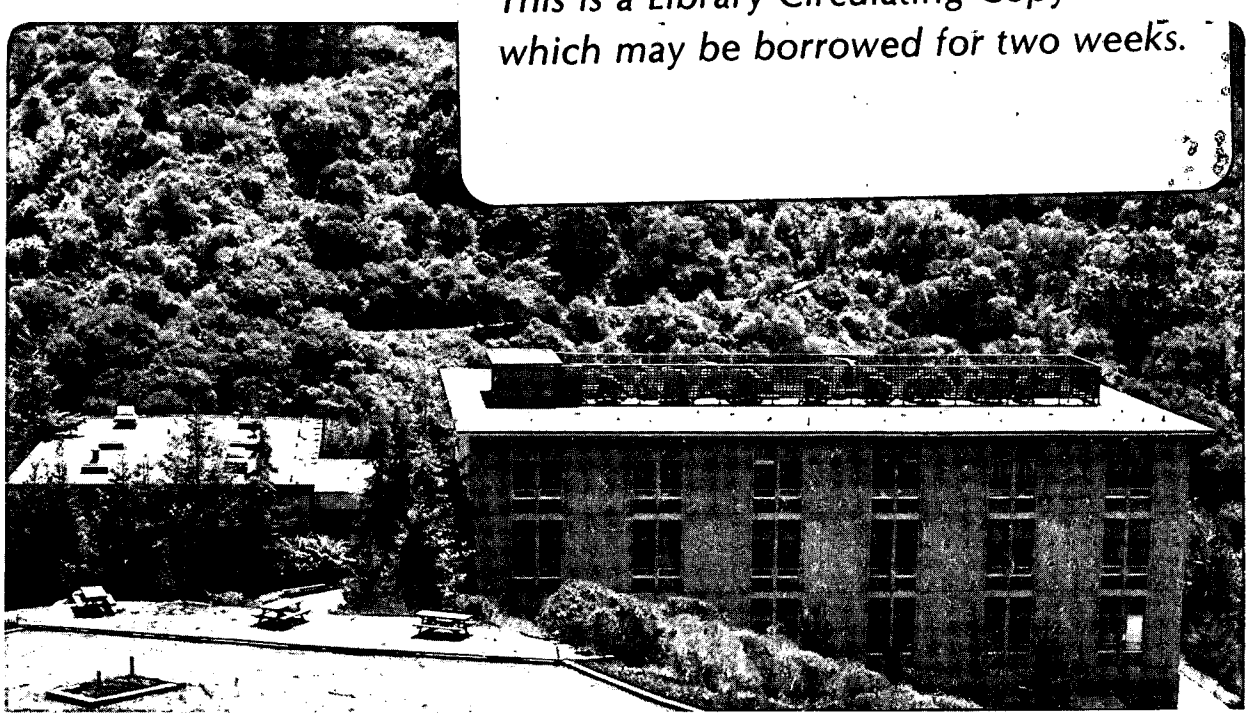

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Resonance Effects on the Inner-Valence Levels of SF_6 in the Photon-Energy Range 52-72 eV

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Abstract

We report the photoionization partial cross section and asymmetry parameter in the 52-72 eV photon-energy range for the inner-valence orbitals ($3t_{1u}$, $2e_g$, and $4a_{1g}$) in gaseous SF_6. These results, combined with those for the (inner valence)/(outer valence) branching ratio, indicate resonant enhancement of the inner-valence levels at ~59 eV photon energy which we associate with the $3t_{1u}$-->e_g shape resonance predicted by MSM-Xα calculations.

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I. Introduction

The SF_6 molecule has provided a classic demonstration of the role played by shape resonances in the absorption and photoionization dynamics of both the valence [1,2] and core [3-9] levels. Particular attention has been paid to the effect of the t_{2g} and e_g "d-type" shape resonances on the gas-phase photoionization cross section and the angular-distribution parameter as a function of photon energy for the SF_6 outer-valence levels [1,2]. At ~23 eV photon energy, a transition has been predicted to occur from the $5t_{1u}$ and $1t_{2u}$ states (binding energy 17.0 eV) to the t_{2g} shape-resonant state [10]. A significant enhancement of the relative cross section for the corresponding peak in photoemission was detected, but there was also an enhancement at the same photon energy for the peaks with binding energies of 15.7 eV ($1t_{1g}$) and 18.6 eV ($3e_g$) [1,2]. Similar behavior has been observed in the photoemission spectra of solid SF_6 [11].

The enhancement of the photoionization cross section for the $1t_{1g}$ and $3e_g$ valence levels at 23 eV cannot be explained within a simple shape-resonance model. First, these transitions from gerade (g) orbitals to the t_{2g} state are not symmetry allowed. In addition, a one-electron model describes the phenomenon as a final-state effect, occurring at approximately the same kinetic energy for each photoemission channel, rather than at the same photon energy [5].

Two explanations for the observed valence peak enhancement in SF_6 have been discussed [2], one invoking autoionization of a discrete state, and the other invoking continuum-continuum coupling at a shape resonance. The first postulates that a one-electron transition from an outer valence orbital to a discrete state (most likely the $5a_{1g} \rightarrow 6t_{1u}$ transition) occurs at ~23 eV photon energy and autoionizes into several continua. The energy for this transition has been estimated by several authors to be ~25 eV [12] and 26.7 eV [2]. Because these estimates did not include hole-screening effects, the possible contribution of this discrete resonance near 23 eV should be considered. This particular resonance, which is below the valence $5a_{1g}$ threshold (26.8 eV), might well be accidentally coincident in energy with the predicted $(5t_{1u} + 1t_{2u}) \rightarrow t_{2g}$ shape resonance, further complicating the interpretation.

The second proposed explanation for the effects near $h\nu$=23 eV involves continuum channel interaction, which allows the t_{2g} shape-resonant continuum state to couple and decay into neighboring continuum levels [2]. Recent K-matrix calculations on N_2 show that continuum-continuum coupling is important near the $3\sigma_g \rightarrow \varepsilon\sigma_u$ shape resonance, producing effects in the photoionization dipole amplitude and asymmetry parameter for the neighboring $2\sigma_u$ valence channel [13]. Qualitatively, the quasibound continuum electron has large amplitude in the core at resonance, enhancing many-electron effects.

An independent experiment which further verifies the complexity of these shape resonances was performed recently on the

photoionization of the sulfur 2p orbital and of a related satellite in SF_6 [14]. It showed that there is a resonant enhancement of both the S 2p main line and satellite at the same photon energy. The resonant feature at this energy had been assigned previously as the S $2p(2t_{1u})$-->e_g shape resonance (196.5 eV) [6-9]. We note that despite the unusual behavior of the e_g shape resonance in S 2p core-level photoemission, there is no evidence for the e_g shape resonance in outer-valence ionization. Clearly, the traditional simple models cannot explain the unusual resonant effects in the valence and S 2p levels of SF_6.

Inner-valence photoemission has been until recently a less established field of study due to the relative inaccessibility of the necessary ionizing radiation (>30 eV) either from lamp sources or traditional monochromators for synchrotron radiation. In addition, cross sections for inner-valence ionization are about an order of magnitude less than for outer-valence ionization. Furthermore, correlation effects in the inner-valence region of molecules can be important in photoelectron spectra [15], making it more difficult to observe resonant effects in individual channels. Even for small molecules like PH_3 [16] and H_2S [16,17], the inner-valence orbitals are highly correlated, giving many more final states (and thus photoemission peaks) than one-electron calculations would predict. The distribution and symmetry of the correlation states in the inner-valence region of SF_6 will mediate the effect of shape resonances.

To supplement our understanding of the strong multi-electron shape resonant effects in the outer-valence and S 2p core-level photoionization, we have investigated the inner-valence ionization of SF_6. This is the first energy-dependent study for inner-valence photoemission in the vicinity of a predicted shape resonance. We report here the relative partial photoionization cross sections of the inner-valence orbitals in SF_6 including the $2e_g$, $3t_{1u}$, and $4a_{1g}$ states, which have mainly fluorine 2s character [18]. We monitored the behavior of the inner- and outer-valence states through the photon energy range in which a transition from the $3t_{1u}$ inner-valence orbital to the e_g shape resonance is expected (~57 eV), and where the total photoabsorption cross section for SF_6 exhibits a weak maximum [19]. One-electron MSM-Xα calculations show the $3t_{1u}$-->e_g shape resonance at ~15 eV kinetic energy, with no enhancement in the neighboring $2e_g$ and $4a_{1g}$ inner-valence shells [10].

The experiment is described in Sec. II, and the results are presented and discussed in Sec. III. Conclusions appear in Sec. IV.

II. Experimental

The experiment was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) using the new 4° line grazing-incidence "grasshopper" monochromator. Photoelectrons were detected at 0° and 54.7° relative to the photon polarization using the double-angle

time-of-flight method [20-22]. This method takes advantage of the time structure of the SPEAR storage ring, and the high collection efficiency of the time-of-flight technique allows the measurement of photon-energy dependent intensities even for low cross-section peaks, in this case from inner-valence photoemission. The relative partial cross section $\sigma(h\nu)$ and angular-distribution asymmetry parameter $\beta(h\nu)$ are obtained assuming the dipole approximation and Yang's theorem [23]:

$$\frac{d\sigma(h\nu,\theta)}{d\Omega} = \frac{\sigma(h\nu)}{4\pi} \left[1 + \beta(h\nu)P_2(\cos\theta)\right], \tag{1}$$

where $P_2(\cos\theta)$ is the second Legendre polynomial and θ is the angle of electron emission relative to the photon polarization direction.

For the SF_6 measurements, a 1500-Å-thick silicon window separated the sample-chamber (10^{-4} torr) from the monochromator (10^{-10} torr). Photoelectron spectra were taken in the photon energy range $52 \leq h\nu \leq 72$ eV using 1200 line/mm and 600 line/mm holographically ruled gratings. The analyzer resolution was about 3 percent of the electron kinetic energy. The photon resolution varied from 0.3 to 0.6 eV. Calibration of the analyzer transmission and relative analyzer efficiency as functions of kinetic energy were performed by measuring the known partial cross sections and asymmetry parameters for the 2s and 2p levels of Ne [24]. The photon intensity was monitored by a sodium salicylate scintillator with an optical photomultiplier tube (RCA 8850), and the relative sample pressure was recorded with a capacitance manometer. Error bars in the σ and β plot

are statistical only. We estimate systematic errors of less than 10 percent for σ and ± 0.15 for β.

III. Results and Discussion

A representative time-of-flight (TOF) photoemission spectrum of the inner- and outer-valence levels of SF_6 taken at $\theta=54.7^\circ$ and 60 eV photon energy is shown in Fig. 1. The accepted outer valence ordering is $1t_{1g}$, $5t_{1u}$ + $1t_{2u}$, $3e_g$, $1t_{2g}$, $4t_{1u}$, and $5a_{1g}$ with binding energies of 15.7, 17.0, 18.6, 19.7, 22.5, and 26.8 eV respectively [2]. For our experimental conditions, the first five outer-valence orbitals (labelled 'val' in Fig. 1) are unresolved. In contrast, the $4t_{1u}$ and $5a_{1g}$ peaks are well separated. For the inner-valence levels, the $2e_g$ (binding energy 39.3 eV) and $3t_{1u}$ (binding energy 41.2 eV) levels overlap almost completely; the much less intense $4a_{1g}$ peak (binding energy 44.2 eV) is quite well resolved from the ($3t_{1u}$ + $2e_g$) peak [18].

The cross section and asymmetry parameter for the sum of the inner-valence levels are shown in Fig. 2. There is a clear enhancement in the cross section, peaking near 58-60 eV. This increase corresponds to the small effect in the total photoabsorption cross section at the same energy [19]. There is no corresponding detectable effect in the inner-valence β (Fig. 2, bottom). Due to the scatter in our data, the possible minimum in β near 60 eV should be considered tentative. The asymmetry parameter appears to increase

with energy.

The (inner valence)/(outer valence) intensity branching ratio is shown in Fig. 3. The data are consistent with inner-valence enhancement superimposed on a smoothly increasing branching ratio. The relative increase of inner-valence intensity at higner energy is well known. It has been observed in H_2O [25] and is indicative of the increasing importance of lower l states at higher energy (the inner-valence orbitals are mainly F 2s). In atomic Ne, the $\sigma(2s)/\sigma(2p)$ branching ratio demonstrates similar behavior [18].

Though the photon-energy range in which the inner-valence states are enhanced, there is no appreciable enhancement in the cross section for the outer-valence levels. We evaluated the individual cross sections for the 'val' peak (see Fig. 1) and for the $5a_{1g}$ and $4t_{1u}$ peaks. These cross sections show the same trend, smoothly decreasing in the photon-energy range under investigation. These results are consistent with previous total photoabsorption data which show an overall decrease in the photon-energy range 52-72 eV [19]. Our data show a decrease for the cross section for all of the first five valence levels together, which is the predominant contribution to the total cross section.

IV. Conclusions

An enhancement is observed for the sum of the inner-valence ($3t_{1u}$, $2e_g$, and $4a_{1g}$) photoionization cross sections. We

observe no distinct evidence of coupling to the outer-valence levels. The relative contributions of the $3t_{1u}$, $2e_g$, and $4a_{1g}$ states to the resonant enchancement cannot be assessed on the grounds of our experimental findings; thus, we cannot rule out participation of the $2e_g$ and $4a_{1g}$ states in the resonance. It is likely, though, that the observed cross-section effects are due to the e_g shape resonance. However, many-body interactions in the inner-valence region will complicate the correlated photoemission final states, which are unresolved or have low intensity in our experiment, and their coupling to the e_g resonance.

Acknowledgements

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Figure Captions

Fig. 1 TOF photoemission spectrum of SF_6 measured at $h\nu$=60 eV and θ=54.7°. The peak labelled 'val' consists of the unresolved outer-valence orbitals $1t_{1g}$, $5t_{1u}$, $1t_{2u}$, $3e_g$, and $1t_{2g}$.

Fig. 2 Relative partial cross section (σ) and asymmetry parameter (β) for the combination of the $3t_{1u}$, $2e_g$, and $4a_{1g}$ inner-valence orbitals of SF_6.

Fig. 3 The branching ratio for the inner-valence intensity relative to the outer-valence intensity.

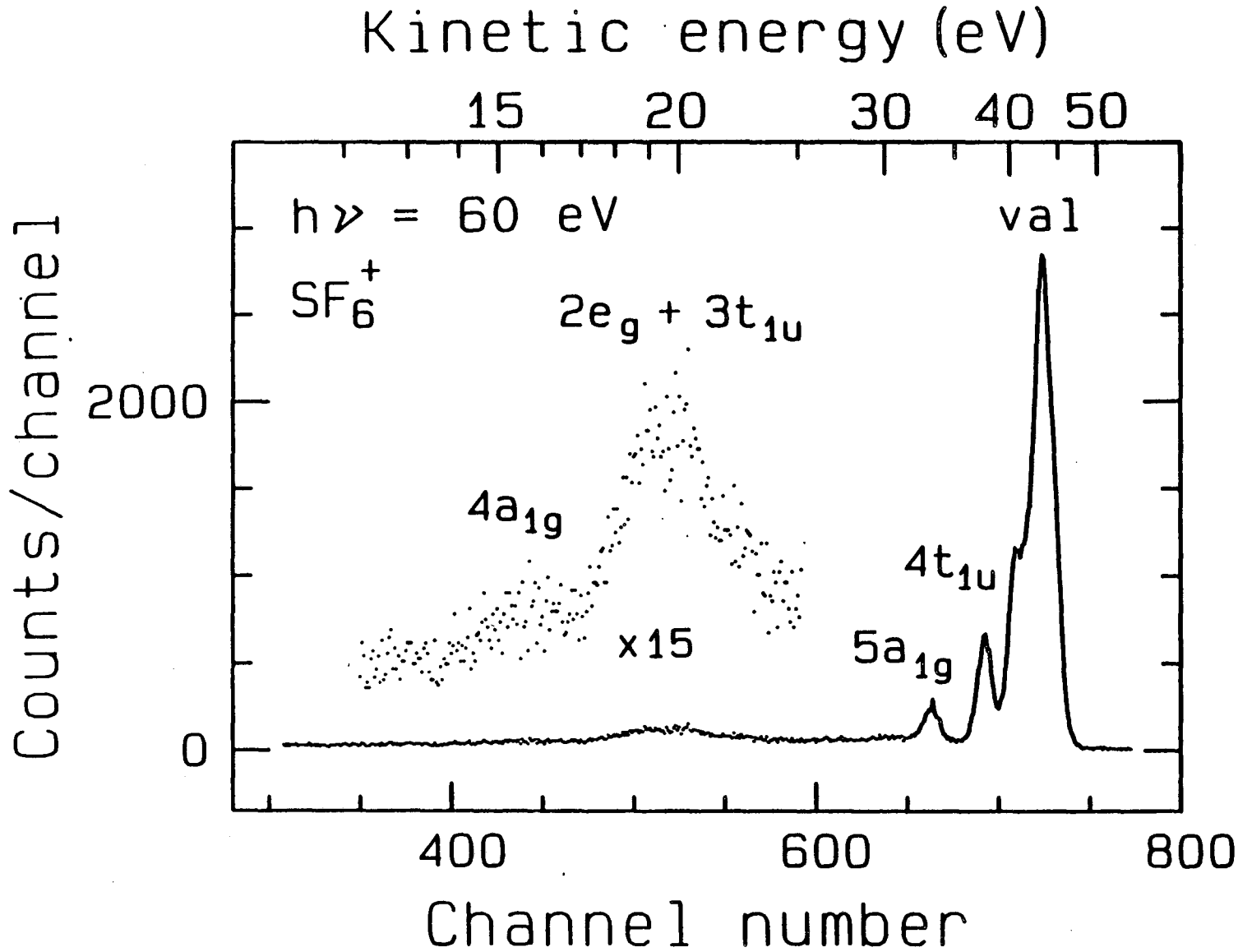

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Figure 1

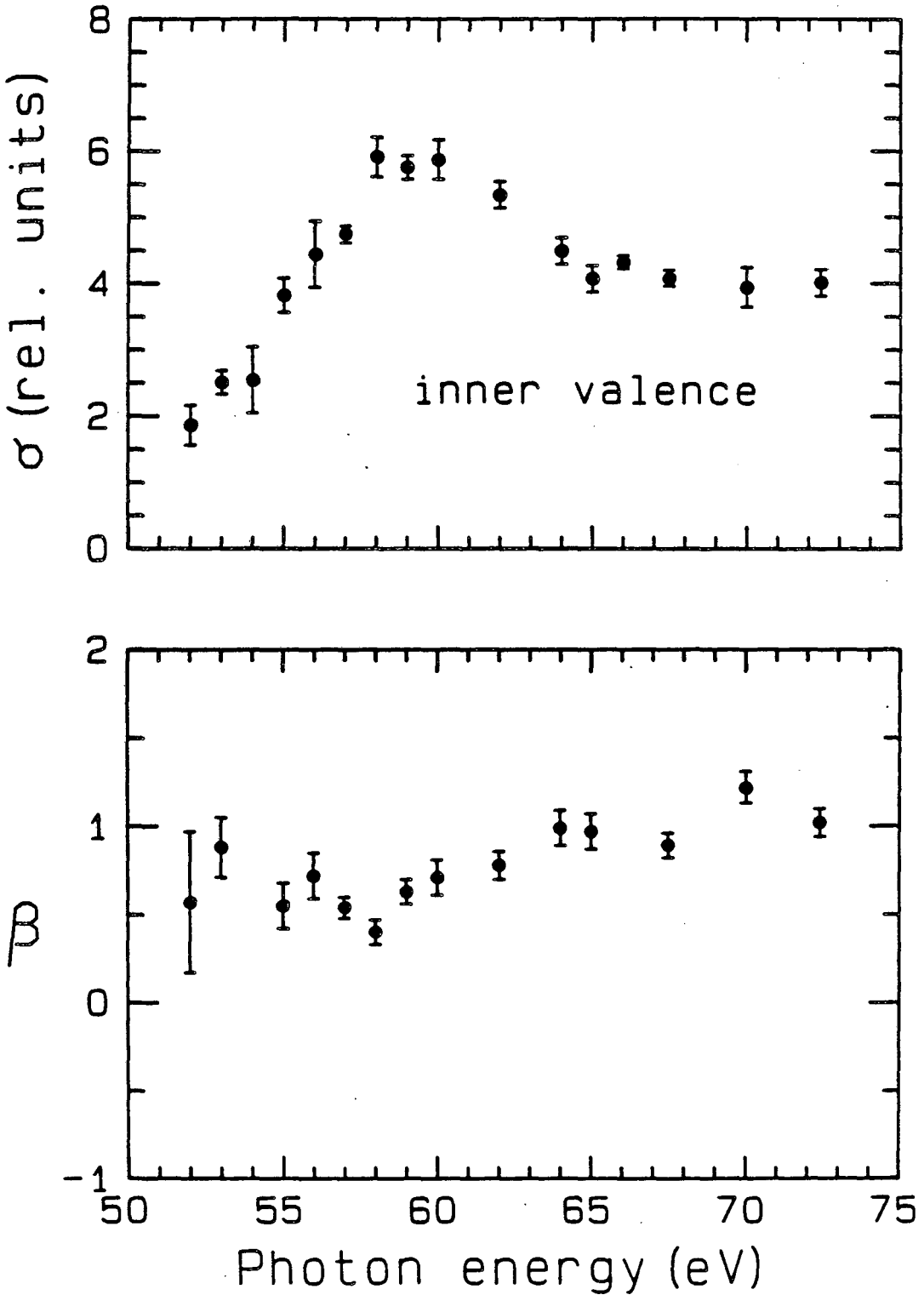

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Figure 2

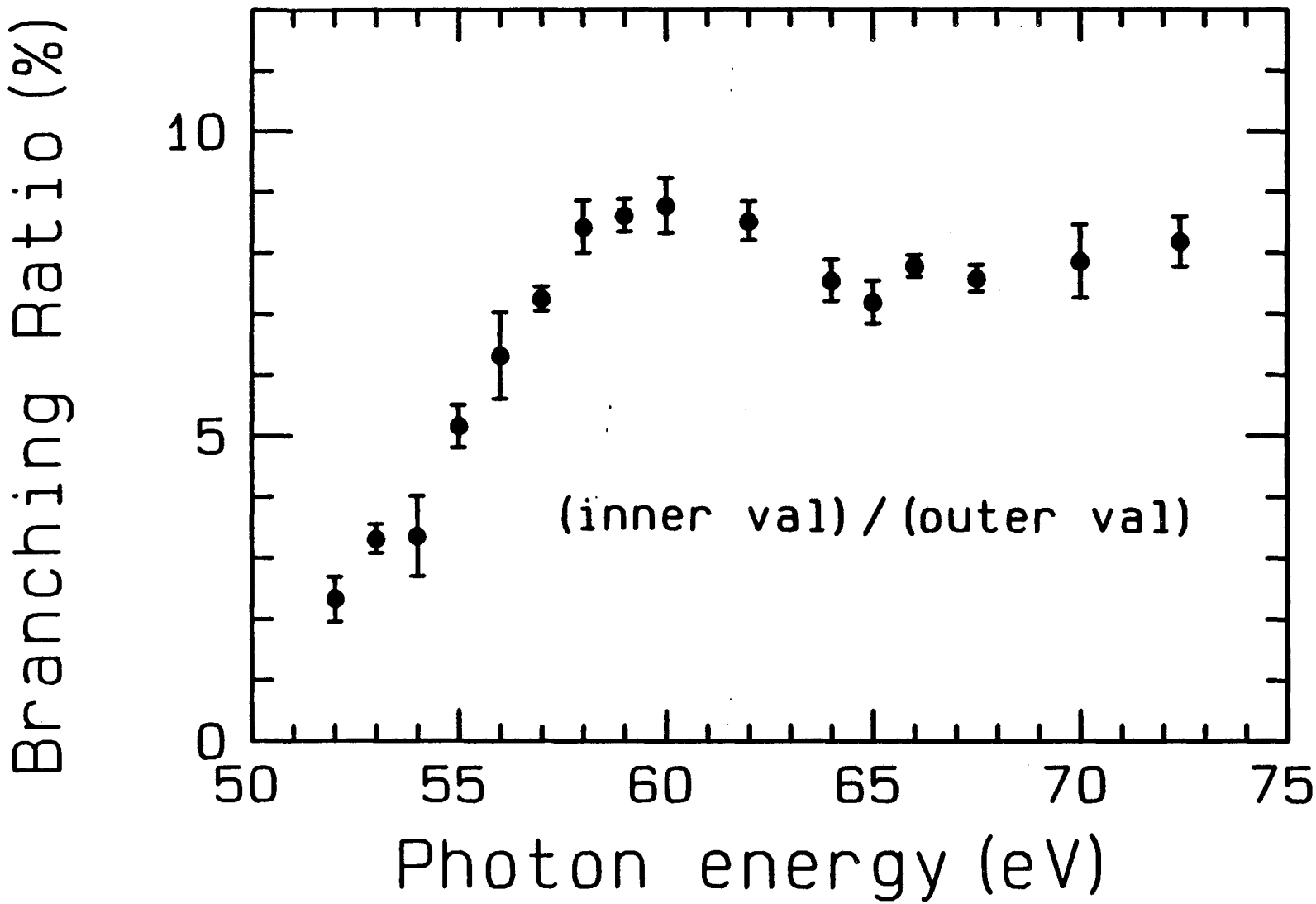

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Figure 3

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