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NEAR-THRESHOLD BEHAVIOR OF THE K-SHELL SATELLITES IN CO

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Abstract

The study of photoelectron satellites in the near-threshold region is important for differentiating among various electron correlation mechanisms. For CO, which is a prominent test case for theories describing electron correlation effects, the threshold and near-threshold branching ratios (BR) of the K-shell satellites were measured. Eight different C 1s satellite states were identified, showing very complex threshold behavior. Resonance-like behavior of the $(2\sigma)^{-1}(1\pi)^{-1}(2\pi^*)^1(S'=1)$ satellite BR agrees with recent theoretical calculations. The observed energy dependence of the singlet $(2\sigma)^{-1}(1\pi)^{-1}(2\pi^*)^1$ satellite compares less well with the calculations. Three $^2\Sigma^+$ satellites with a $(2\sigma)^{-1}(5\sigma)^{-1}(n\sigma)^1$ configuration have a constant satellite BR over the energy range studied. Three 2σ satellites, which have been assigned as pure conjugate shake-up states, have intensity only near threshold. The threshold spectrum above the O 1s ionization threshold consists of two distinct groups of satellites. Conjugate shake-up transitions contribute to the intense feature centered at 551 eV binding energy, which is not observed above its threshold. Two $^2\Sigma^+$ satellites, which have been described by configuration interaction of $(1\sigma)^{-1}(5\sigma)^{-1}(n\sigma)^1$ states with a singlet $\pi\pi^*$ state, show indications of shape resonance-like behavior.

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I. Introduction

During the past two decades, a great deal of experimental and theoretical work was devoted to the study of the core-shell photoionization in diatomic molecules. Among them, CO has been used as an important test case for understanding the complex processes involving the ionization of core-shell electrons. The ionization of K-shell electrons in CO is accompanied by excitation and ionization of valence electrons, which manifest themselves in the photoelectron spectrum as pronounced shake-up and shake-off structure at energies near the corresponding 1s main line. A high-resolution C 1s satellite spectrum of CO excited by monochromatized Al Kα x-rays shows more then ten discrete lines of different widths, with intensities varying between 0.4 - 4.8% of the main-line intensity [1,2]. The first two, and by far the most intense, C 1s satellite peaks lie 8.34 and 14.88 eV above the C 1s line with relative intensities of 2.3 and 4.8% and widths of 1.3 and 2.0 eV, respectively [2]. On the basis of extended configuration interaction calculations [3], these two satellite peaks have been assigned to $(2\sigma)^{-1}(1\pi)^{-1}(2\pi^*)^1$ transitions with the spin of the π and π^* electrons coupled to an intermediate triplet (S'=1) or singlet (S'=0) state. A fourth-order Green's function method predicted the relative intensities of the triplet and singlet $\pi\pi^*$ satellites, in agreement with experiment [4]. At high excitation energies, the satellite intensity is determined solely by the bound-state wave functions and is proportional to the spectroscopic factor.

At excitation energies close to the satellite threshold, (e,2e) coincidence measurements showed a strong increase of up to 10% in the relative intensity of the triplet $\pi\pi^*$ satellite [5]. This surprising result was explained by a conjugate shake-up transition, e.g. a dipole excitation of the 2σ electron to the $2\pi^*$ orbital accompanied by a monopole shake-off of the 1π electron. Depending on the amount of overlap between the continuum and ground states, a conjugate shake-up transition can contribute significantly to the satellites intensity near threshold. Its role will decrease quickly with increasing photon energy. Near-threshold studies of the C 1s satellite intensities were performed with variable photon energy at a synchrotron light source [6]. Over the photon energy range of 350 - 400 eV, the intensity of the singlet $\pi\pi^*$ satellite decreases monotonically with decreasing photon energy. The triplet $\pi\pi^*$ satellite shows an increase of its relative intensity with decreasing photon energy in the range of 320 - 400 eV, goes through a maximum at $\approx$ 320 eV, and decreases toward threshold. In contrast to the high-energy limit, the triplet $\pi\pi^*$ satellite has a greater intensity at threshold than the singlet satellite. The crossing point is at about 363 eV. In Ref. 6, the enhanced relative intensity of the $\pi\pi^*$ satellite was attributed to a shape resonance rather than to a conjugate shake-up process. Later experiments in the same

photon-energy range did not confirm the resonance-like structure of the triplet $\pi\pi^*$ satellite intensity [7]. Instead, a monotonic increase of the relative satellite intensity was observed as the photon energy decreases toward the satellite threshold. In Ref. 8, the experimental data were compared with calculations based on the relaxed-core Hartree-Fock approximation. The energy-dependent intensities of the singlet and triplet $\pi\pi^*$ satellite were explained by strong interference effects between the direct and conjugate contributions to the transition moment in the threshold region. Constructive interference in the $k\pi$ subchannel led to a dramatic increase of the triplet $\pi\pi^*$ satellite intensity. For the singlet $\pi\pi^*$ satellite, destructive interference led to a small satellite intensity near threshold. The calculations show strong σ shape resonances in both satellite channels about 10 eV above threshold, which is in clear disagreement with the experiments. It was, however, mentioned by the authors of Ref. 8 that the calculated position and even the occurrence of these resonances may well be artifacts of their calculation.

Zero electron kinetic energy (ZEKE) spectra taken across the C 1s ionization threshold of CO showed a relative intensity of the triplet $\pi\pi^*$ satellite nearly five times larger than at 1487 eV photon energy [9]. No peak was detected at the photon energy of the singlet $\pi\pi^*$ satellite and its threshold intensity was estimated to be less than 2%. A small shoulder on the high-binding-energy side of the triplet $\pi\pi^*$ satellite was attributed to the appearance of satellite states of other than $^2\Sigma^+$ symmetry, which are absent at high photon energies. High-resolution ZEKE spectra of the energy region of the triplet $\pi\pi^*$ satellite revealed a peak lower in energy than the lowest-energy $^2\Sigma^+$ state [10]. It was concluded that the observed intensity increase in the region of the triplet $\pi\pi^*$ satellite results in part from the opening of channels to other electronic states.

The high-resolution spectrum of the O 1s satellites excited with 1487 eV photons has a completely different structure than the corresponding part of the C 1s spectrum [2]. The O 1s satellite spectrum is dominated by three closely spaced satellite lines centered at 17 eV above the main line. A fourth-order Green's function calculation of the intensities and shake-up energies predicted the triplet $(1\pi)^{-1}(2\pi^*)^1$ satellite to lie 14.9 eV above the O 1s line, with such a small intensity that it will not be observed at high photon energies [4]. Moreover, at least two intense satellite states of $(5\sigma)^{-1}(n\sigma^*)^1$ character with large π-π^* admixtures were calculated, instead of one distinct singlet-coupled $\pi\pi^*$ state. The configuration interaction between the $\pi\pi^*$ (S'=0) and $\sigma\sigma^*$ states was explained qualitatively on the basis of the electron density distributions of the 1π and 5σ orbitals [4]. For the π-π^* excitation, a charge transfer from O to C results in an anti- screening of the O 1s hole and a larger shake-up energy for the corresponding satellite state. The 5σ orbital in CO is localized more toward C. Thus, the 5σ-$n\sigma^*$ excitation led to a screening of the O 1s

hole and lowering of the shake-up energy in this satellite channel. As a consequence, the singlet $\pi\pi^*$ and $\sigma\sigma^*$ satellites are pushed closer together in energy.

The branching ratio (BR) of this group of satellites has been studied in the range of 20 - 100 eV above threshold with low resolution [11]. The data showed a slight decrease of the BR toward threshold. At 80 eV above threshold, the unresolved group of satellites reached the combined intensity of the first three satellite states observed at 1487 eV, indicating a behavior between the adiabatic and sudden limits.

In the earlier near-threshold studies [6, 7] of the C 1s triplet $\pi\pi^*$ satellite, the monochromator resolution precluded the observation of distinct electronic states. It was the aim of this work to study the near-threshold behavior of the C 1s triplet and singlet $\pi\pi^*$ satellite states with high resolution. In addition to the $\pi\pi^*$ satellites, we report on the near-threshold behavior of additional C 1s satellites at higher binding energy. The O 1s satellites in CO were also studied in the near-threshold region.

The outline of this paper is as follows. Section II describes the experiment. Section III contains the results and discussion of the C 1s and O 1s satellites. Finally, Sec. IV gives the conclusions.

II. Experimental

The experiments were performed at the Spherical Grating Monochromator (SGM) [12], BL 6-1, installed at a 54-pole wiggler/undulator at the Stanford Synchrotron Radiation Laboratory (SSRL). During our experimental run, SSRL operated in the 4x1 timing mode, where four electron bunches in the storage ring were spaced by approximately 195 ns. To cover the complete threshold region, low kinetic-energy electrons were studied with the time-of-flight (TOF) method. The threshold time-of-flight (TTOF) analyzer, which is described in detail in Ref. [13], was used in two particular modes. In the first one, photoelectrons with a kinetic energy of 0 - 30 meV were extracted by a weak electric field from the interaction region and energy-analyzed according to their flight times from the interaction region to the detector. In the second mode, photoelectron spectra were taken, in which the electrons travel through a field-free region to the detector. In this case, the TOF analyzer has a slowly varying transmission function, which is determined for every experimental run [14]. In order to measure electron intensities which are independent from angular distribution effects, the angle between the electric vector and the analyzer axis was fixed at 54.7°.

To calibrate the energy scale and to determine the resolution of the monochromator, a

photoionization (PI) spectrum was recorded simultaneously with the ZEKE scan. The PI spectra was measured as the total PI current, using a two-plate ionization gas cell mounted downstream from the chamber [15]. Two 1000 Å thick Ti windows separated the chamber from the gas cell and the ultrahigh vacuum of the monochromator. No correction was made for the weak Ti 2s absorption edge at 560.9 eV, which fell in the experimental energy range. The spectra were normalized to the photoemission current measured from a Au grid upstream from the chamber.

With a backing pressure of 50 torr in the effusive gas source, the background pressure in the chamber was less than 5×10^{-5} torr. A pressure of 10-20 mtorr was maintained in the photoionization gas cell.

The vertical openings of the entrance and exit slits of the SGM were 100 and 75 μm, respectively, which corresponds to a theoretical resolution of 170 meV at 296 eV. A fit of the PI and ZEKE spectrum gave a Gaussian contribution of 170 and 225 meV, respectively. The TOF analyzer resolution, ΔE, was 3% of the electron kinetic energy.

Before making the peak analysis of the photoelectron spectrum, the TOF spectrum was converted into a kinetic-energy spectrum and corrected for the analyzer efficiency. The kinetic energies of the photoelectron lines in the TOF spectrum were determined on the basis of the corresponding binding energies of C 1s, O 1s, 3σ, 4σ, and 5σ in CO which are 296.19, 542.57 [2], 37.3, 19.69, and 14.01 eV [16], respectively. The kinetic energies of the C KVV B-1 and O KVV B-5 Auger lines in CO were taken from Ref. 17.

The analyzer efficiency was determined by dividing the C 1s/ C KVV intensity ratios from Ref. 18 and 19 by the values from our measurement. The two data sets for the analyzer efficiency agreed within 3%.

To obtain a consistent fit for all ZEKE and TOF spectra, we used an asymmetric Gaussian line shape for the satellite peaks. The asymmetry takes account of vibronic structure and the post-collision interaction. The intensity of the 1s lines was determined by integrating over the corresponding spectral range.

III. Results and Discussion

A. C 1s satellites

Figure 1 shows the ZEKE and PI scans across the C 1s ionization threshold. Fig. 2 contains photoelectron spectra taken at several photon energies above this threshold. The energies of the satellite peaks observed at a photon energy of 1486.6 eV appear as vertical

bars [2]. We also note that C 1s photoelectron spectra at 320 and 340 eV with high resolution in the triplet $\pi\pi^*$ satellite region have been measured recently [20]. The assignments of the satellite peaks are based on the comparison of their energy and intensity variations with theoretical results. The satellites which are observable at high photon energies must have $^2\Sigma^+$ symmetry -- the same symmetry as the main C 1s line. According to the model of the sudden limit [21], satellites of other than $^2\Sigma^+$ symmetry should have no intensity at high photon energies. These "monopole-allowed" satellite states have been assigned previously on the basis of large configuration interaction (CI) calculations [3] and a fourth-order-perturbation Green's function calculation [4]. The assignment of the monopole satellites and a comparison of the theoretical and experimental shake-up energies is given in Table 1. It is interesting to note that the satellites assigned as $\pi\pi^*$ correlation states have a much broader and more asymmetric lineshape than the $\sigma\sigma^*$ satellites.

As can be seen from Fig. 3, the five observed satellites with $^2\Sigma^+$ symmetry show different threshold behavior. Within the accuracy of our measurement, the intensities of the $(2\sigma)^{-1}(5\sigma)^{-1}(n\sigma)^1$ satellites at 314.3, 315.7, and 316.6 eV does not change with photon energy and is about the same as was reported in Ref. 2 for 1486.6 eV photon energy. Specifically, the average BR values for these three satellites over the photon energy range 315-340 eV (the last four points in Fig. 3) are 1.5, 1.1, and 1.3%, respectively, compared with 1.9, 1.1, and 1.6% from Ref. 2. This behavior is predicted for satellites arising due to CI in the neutral ground state and/or the final ionic state [22, 23] and has been observed, for example, in the case of some Ne valence and K-shell satellites [24-26].

The different threshold behavior of the two $\pi\pi^*$ satellites at 304.1 and 311.4 eV, in which where the two electrons in the π and π^* orbitals form an intermediate triplet (S'=1) and singlet (S'=0) state, respectively, has been explained by calculations using the relaxed-core Hartree-Fock (RCHF) approximation [8]. For both satellite states, the kσ channel shows a σ^* shape resonance associated with quasibound double excitations of the type $(1s)^{-1}(1\pi)^{-1}(2\pi)^1(\sigma^*)^1$, where σ^* is the unoccupied valence-type σ orbital derived from the 2p atomic orbitals. At threshold, negative and positive interference in the kπ channel between the direct and conjugate parts of the transition moment causes a substantial reduction of the S'=0 $\pi\pi^*$ satellite and a dramatic enhancement of the S'=1 $\pi\pi^*$ satellite.

In the energy region of the triplet $\pi\pi^*$ satellite, only the satellite peak at 304.9 eV shows the same threshold behavior as predicted by calculations [8, 27] and therefore has been assigned as the S'=1 $\pi\pi^*$ satellite. In Fig. 4, the BR of the triplet $\pi\pi^*$ satellite is compared with other experimental and theoretical data. Previously measured BRs are much larger than our data because the earlier resolution was not sufficient to separate the different components of the group of satellites centered at 305 eV. The combined intensity of all

three satellite states agrees with the data from Ref. 7. The measured height and width of the σ^* shape resonance in the BR of the triplet satellite channel appear to agree with the RCHF calculations [8], although our experimental evidence comes from one high point. The position of the σ^* shape resonance differs by 5 eV. In Ref. [8] it was mentioned that the theoretical position of the σ^* shape resonance in the C 1s channel and therefore in the corresponding satellite channel is about 2-3 eV too high. More recent calculations in a multichannel configuration-interaction (MCCI) approximation [27] predicted the position of the σ^* shape resonance around 318 eV with a much greater asymmetry toward higher photon energy. The theoretical position of the σ^* shape resonance in the 2σ core hole channel is also about 4 eV higher than the experimental value [19]. Possible strong modulations of the BR near threshold due to autoionizing Rydberg states cannot be excluded by our experimental results because of the low density of measured points.

In Fig. 5, the experimental and theoretical BR for the singlet $\pi\pi^*$ satellite at 311.4 eV are shown. Our data show a weak resonance close to the position predicted by calculations [8, 27]. But the amplitude of the resonance is much smaller in the experiment than that calculated by the RCHF and the MCCI methods.

The satellite state 0.7 eV below the triplet $\pi\pi^*$ satellite ("Peak 1"), which has a large intensity enhancement toward threshold (see Fig. 3), could be of $^2\Pi$ symmetry, associated with the configuration $(2\sigma)^{-1}(5\sigma)^{-1}(2\pi)^1$ (S'=1). For this electronic state, the fourth-order Green's function calculations [4] gave a shake-up energy 0.56 eV below the first monopole-allowed satellite. Within the equivalent-core model, a Franck-Condon analysis of the lowest binding energy satellite supports its assignment as a $^2\Pi$ state [10]. The separation between the triplet and singlet $^2\Pi$ satellites is predicted to be 0.76 eV, much smaller than for satellites of $^2\Sigma^+$ symmetry.

It is not possible to assign the satellite state at 306.4 eV unambiguously without calculations of its intensity near threshold . In Ref. 4, the shake-up energies of four monopole-forbidden satellite states associated with the $(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^1$ configuration are given as 9.7, 9.8, 11.1, and 11.4 eV for $^2\Delta$(S'=1), $^2\Sigma^-$(S'=1), $^2\Delta$(S'=0), and $^2\Sigma^-$(S'=0), respectively. According to the results in Ref. [8], the cross section for these states are given by $6\sigma_0$, $3\sigma_0$, $2\sigma_0$, and σ_0, respectively, where σ_0 is the effective conjugate cross section for the singlet $\pi\pi^*$ satellite of $^2\Sigma^+$ symmetry. Since the value of σ_0 is an order of magnitude smaller than the value for the triplet $\pi\pi^*$ satellite of $^2\Sigma^+$ symmetry and decreases quickly above threshold, it seems quite likely that only the most intense $^2\Delta$(S'=1) satellite at 9.7 eV might be observed experimentally, and/or that one or more of the other three satellites in this group might be combined with this peak.

Based on the statistical ratios of the satellite multiplets given above, the satellite peak

observed at 309.3 eV is probably of $^2\Pi$ symmetry [28]. The theoretical shake-up energies of 13.6 and 14.3 eV for the triplet and singlet satellites associated with a $(2\sigma)^{-1}(4\sigma)^{-1}(2\pi)^1$ configuration, respectively, are close to the experimental value of 13.1 eV.

B. O 1s satellites

Fig. 6 shows the ZEKE and PI scans across the O 1s ionization threshold. The main feature in the ZEKE spectrum is the O 1s main line, which is asymmetrically broadened and shifted toward higher photon energy by post-collision interaction. Below the O 1s threshold, several electron/hole (1h-1e) Rydberg states can be observed in both the ZEKE and PI spectra. According to Ref. [29], these states can be assigned with increasing photon energy as $3p\pi$, $4p\pi$, and higher unresolved $np\pi$ members of the Rydberg series. Above the O 1s threshold, two-electron/two-hole (2e-2h) doubly excited neutral states can be seen as weak structures very close to threshold. Their positions coincide with weak structures in the PI signal which lie on top of the broad σ^* shape resonance. The CI calculations of Ref. [30] predicted several doubly-excited states with a $1\sigma^{-1}5\sigma^{-1}2\pi^1 n\pi^1$ configuration at photon energies near threshold.

The broad structure between 547 and 553 eV in the ZEKE spectrum has more than one contribution. A weak peak at 8 eV above the O 1s threshold observed with Al Kα excitation has been identified not as a satellite state but as an inelastic-loss feature [2]. The $1\sigma^{-1}5\sigma^{-1}2\pi^1 n\pi^1$ Rydberg series will lead to an ionization threshold of the corresponding 2h-1e satellite state. A fourth-order Green's function calculation gave a shake-up energy of 5.03 and 8.71 eV for the two lowest correlation state satellites of $^2\Pi$ symmetry with a $1\sigma^{-1}5\sigma^{-2}2\pi^1$ configuration [4]. Thus the intensity of the 8 eV structure can be explained partly by the appearance of correlation satellites of $^2\Pi$ symmetry. As in the case for the C 1s conjugate shake-up satellites, these states can have considerable intensity at their threshold and are not observed at higher photon energies. If only two satellite states were contributing to the intensity of the 8 eV structure, one would expect two asymmetric lines with several eV separation. The poorly resolved observed structure might be caused by another 2h-2e Rydberg series coinciding in energy with the conjugate shake-up satellite states. This conclusion is supported by a recent symmetry-resolved O K-shell photoabsorption measurement of free CO molecules. The conventional photoabsorption spectrum was decomposed into the Σ and Π symmetry channels of the dipole-allowed K-shell excitations of CO [31]. The $\sigma\Pi$ spectrum showed an approximately 3 eV (FWHM) wide resonance centered at 551 eV photon energy with even more intensity than in the $\sigma\Sigma$

channel. A CI calculation predicts a $1\sigma^{-1}5\sigma^{-2}2\pi^2$ configuration of Π symmetry as the main component of the 2h-2e states [30]. The theoretical peak position of 555 eV is 4 eV higher than the experimental peak position. With the overlap of 2h-2e and 2h-1e states, a conjugate shake-up satellite intensity can be estimated to be between 2 - 5% for each satellite. The total relative intensity of the 8 eV structure at its threshold is 16%. Above threshold, only a weak peak of 1 - 2% intensity is observed, at 551.2 eV binding energy (see Fig. 7). In Ref. 2, this peak was attributed to an inelastic scattering effect, which should not contribute significantly to our spectra.

Three peaks were partially resolved at 558.4, 559.7, and 560.5 eV in the ZEKE spectrum. These energies agree well with the shake-up energies for the three most intense satellites at 1487 eV photon energy [2]. In the photoelectron spectra of Fig. 7, the spectral range from 556 to 563 eV was fitted assuming the same number of satellite states, relative energy separation, and corresponding linewidths as observed in the high-resolution spectrum with Al Kα excitation [2]. According to the Green's function calculation of Ref. [4], these satellite states are characterized by strong configuration interaction between $(5\sigma)^{-1}(n5\sigma)^1$ states and singlet-coupled $\pi\pi^*$ states. For this reason, it is not possible to assign a distinct state of mostly $\pi\pi^*$ character, as could be done for the C 1s satellites. Within our experimental error, the BRs of these satellites at threshold are the same or slightly less than at high photon energies (see Fig. 8). The intensity variation of the satellite states around 560 eV has been studied previously in the range of 20 - 100 eV above threshold [32]. The BR of the unresolved group of satellites showed only a small increase from 14 to 17% over this energy range (see Fig. 8). Our higher resolution measurements cover the range below the previous measurements and show indication of a resonance-like structure in the satellite BR at about 8 - 10 eV above the corresponding satellite threshold. This is similar to the results found for some of the C 1s satellites. It is interesting to note that the satellite states at 558.6 and 560.8 eV binding energy, which show the largest $\pi\pi^*$ admixture in the CI calculation, have the strongest shape resonance among the observed 1σ satellites. The next-neighbor satellite states at lower binding energy show only a small variation of their BR with photon energy, which is close to the value for the BR at high photon energy.

IV. Conclusion

We have studied the near-threshold behavior of the K-shell satellites in CO with high resolution. Eight C K-shell satellite states were identified, showing a very complex energy dependence. Three $(2\sigma)^{-1}(5\sigma)^{-1}(n\sigma)^1$ satellites are weakly energy dependent and

probably arise from intrinsic electron correlations. Two satellites at 304.1 and 304.7 eV, which are not observed at high photon energies, are characterized by increasing satellite intensity toward threshold as is typical for dynamic correlation states. The first one has been associated with the $(2\sigma)^{-1}(5\sigma)^{-1}(2\pi)^{1}$ (S'=1) $^{2}\Pi$ configuration. The second could originate from a conjugate shake-up process with a $(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^{1}$ configuration of $^{2}\Delta$, and/or $^{2}\Sigma^{-}$ symmetry.

Most of the previous experimental and theoretical work on the K-shell satellites in CO was focused on the triplet and singlet $(2\sigma)^{-1}(2\pi)^{-1}(2\pi)^{1}$ satellites of $^{2}\Sigma^{+}$ symmetry. In the region of the triplet $\pi\pi^{*}$ satellite, we were able to distinguish among three electronic states. Of these, only the state at 304.9 eV binding energy has the same threshold behavior as the triplet $\pi\pi^{*}$ satellite. The relative intensity of this satellite channel goes through a maximum near 310 eV and has been interpreted as a σ resonance. The resonance in the triplet $\pi\pi^{*}$ satellite occurs 5 - 6 eV above its threshold, which is 2 - 3 eV closer than for the $(2\sigma)^{-1}$ core-hole channel. Two other satellites, at 309.3 and 311.4 eV binding energy, show a resonance-like structure as well, at approximately 11 eV above their threshold, although for the singlet $\pi\pi^{*}$ satellite at 311.4 eV binding energy the resonance is less pronounced than predicted by theory.

The ZEKE spectrum across the O 1s edge in CO showed a surprisingly intense feature around 551 eV binding energy, which is not observed at high photon energy. Based on calculations of the satellite thresholds and symmetry-resolved photoabsorption measurements, this structure has been assigned to overlapping contributions of conjugate shake-up states and 2h-2e Rydberg states of Π symmetry. This structure seems to loose its intensity much faster as any other conjugate shake-up state in CO. Two satellite states at 558.6 and 560.8 eV binding energies, which previously have been attributed to the configuration mixing of a $(5\sigma)^{-1}(n\sigma)^{1}$ transitions with a singlet $(1\pi)^{-1}(2\pi)^{1}$ state, show a shape resonance-like structure at 10 eV above threshold. In this case, the relative position of the resonance from threshold is close to that of the σ shape resonance in the $(1\sigma)^{-1}$ channel.

In summary, the K-shell satellites in CO show a complex intensity variation near threshold, including intrinsic and dynamic electron correlation effects and resonances in several satellite channels. For a better understanding of the involved processes, more theoretical calculations are clearly needed for the 2σ satellites other than $(2\sigma)^{-1}(1\pi)^{-1}(2\pi^{*})^{1}$(S'=0,1) and for all the 1σ satellites. Further experimental mapping of satellite branching ratios and angular asymmetry parameters in small energy increments near threshold are also desirable, in order to obtain additional information for the assignment of the satellites and to observe narrow autoionizing structures, which have been predicted for

the $(2\sigma)^{-1}(1\pi)^{-1}(2\pi^*)^1(S'=1)$ satellite channel.

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Figure Captions

1. ZEKE spectrum across the C 1s threshold in CO and the corresponding PI spectrum (solid line). The solid line in the ZEKE spectrum is the fit to the data points. The individual peaks are shown as dashed lines. The vertical lines above the ZEKE spectrum mark the experimental and theoretical satellite thresholds from Refs. 2 and 4, respectively.

2. TOF photoelectron spectra of CO at 315.1, 320.1, and 325.1 eV photon energy. All spectra are normalized to equal C 1s line intensity. The solid line is a fit to the data. The individual peaks are shown as dashed lines.

3. Satellite branching ratios of the C 1s satellites at 304.1 (■), 304.9 (▲), 306.4 (♦), 309.3 (□), 311.4 (Δ), 314.3 (o), 315.7 (⧖), and 316.6 (⋈) eV. The branching ratios derived from the ZEKE spectra were scaled to the C 1s intensity at the photon energy of the satellite's threshold by using the data from Ref. 32.

4. Comparison of the present experimental $(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^{1}$ (S'=1) satellite branching ratio with other experimental and theoretical data. Experiment: —●— satellite at 304.9 eV; ---●--- sum of the satellites at 304.1, 304.9, and 306.4 eV; o, Ref. 9; Δ, Ref. 6; ◊, Ref. 7. Theory: -------, relaxed-core Hartree-Fock, Ref. 8; ——, multichannel configuration interaction, Ref. 27.

5. Comparison of the present experimental $(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^{1}$ (S'=0) satellite branching ratio with other experimental and theoretical data. Experiment: —●— satellite at 311.4 eV; Δ, Ref. 6; ◊, Ref. 7. Theory: -------, relaxed-core Hartree-Fock, Ref. 8; ——, multichannel configuration interaction, Ref. 27.

6. ZEKE spectrum across the O 1s threshold in CO and the corresponding PI spectrum (solid line). The solid line in the ZEKE spectrum is the fit to the data points. The individual peaks are shown as dashed lines. The vertical lines mark the experimental and theoretical satellite thresholds from Ref. 2 and 4, respectively.

7. TOF photoelectron spectra of CO at 558.9, 569.4, 573.4, and 583.2 eV photon energy. All spectra are normalized to equal O 1s line intensity. The solid line is a fit to the data. The individual peaks are shown as dashed lines.

8. Comparison of the present experimental O 1s satellite branching ratios with other experimental data. Experiment: —▲— satellite at 557.5 eV; —♦— satellite at 558.6 eV; —●— satellite at 559.9 eV; --⋈-- satellite at 560.8 eV; —⧖— satellite at 562.9 eV; ---●--- sum of both satellites; ◊, Ref. 11. The marks in the lower right corner indicate the BR for the corresponding satellites with Al Kα excitation [2].

Table I. Binding energy of the C 1s electron correlation states in CO.

		Experiment		Theory
Peak	Assignment	This work	Ref. 2	Ref. 4
0	$(2\sigma)^{-1}\ ^2\Sigma^+$	296.2(1)	296.19	296.08
1	$(2\sigma)^{-1}(5\sigma)^{-1}(2\pi)^1(S'=1)\ ^2\Pi$	304.13(8)		304.52
2	$(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^1(S'=1)\ ^2\Sigma^+$	304.86(6)	304.53(6)	305.19
3	$(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^1\ ^2\Delta,\ ^2\Sigma^-$	306.4(3)		305.82-307.50
4	$(2\sigma)^{-1}(4\sigma)^{-1}(2\pi)^1\ ^2\Pi$	309.29(8)		309.66-310.42
5	$(2\sigma)^{-1}(1\pi)^{-1}(2\pi)^1(S'=0)\ ^2\Sigma^+$	311.4(1)	311.07(6)	313.20
6	$(2\sigma)^{-1}(5\sigma)^{-1}(6\sigma)^1(S'=1)\ ^2\Sigma^+$	314.29(5)	314.04(5)	315.97
7	$(2\sigma)^{-1}(5\sigma)^{-1}(6\sigma)^1(S'=0)\ ^2\Sigma^+$	315.68(4)	315.41(5)	317.26
8	$(2\sigma)^{-1}(5\sigma)^{-1}(7\sigma)^1(S'=1)\ ^2\Sigma^+$	316.62(5)	316.28	317.72

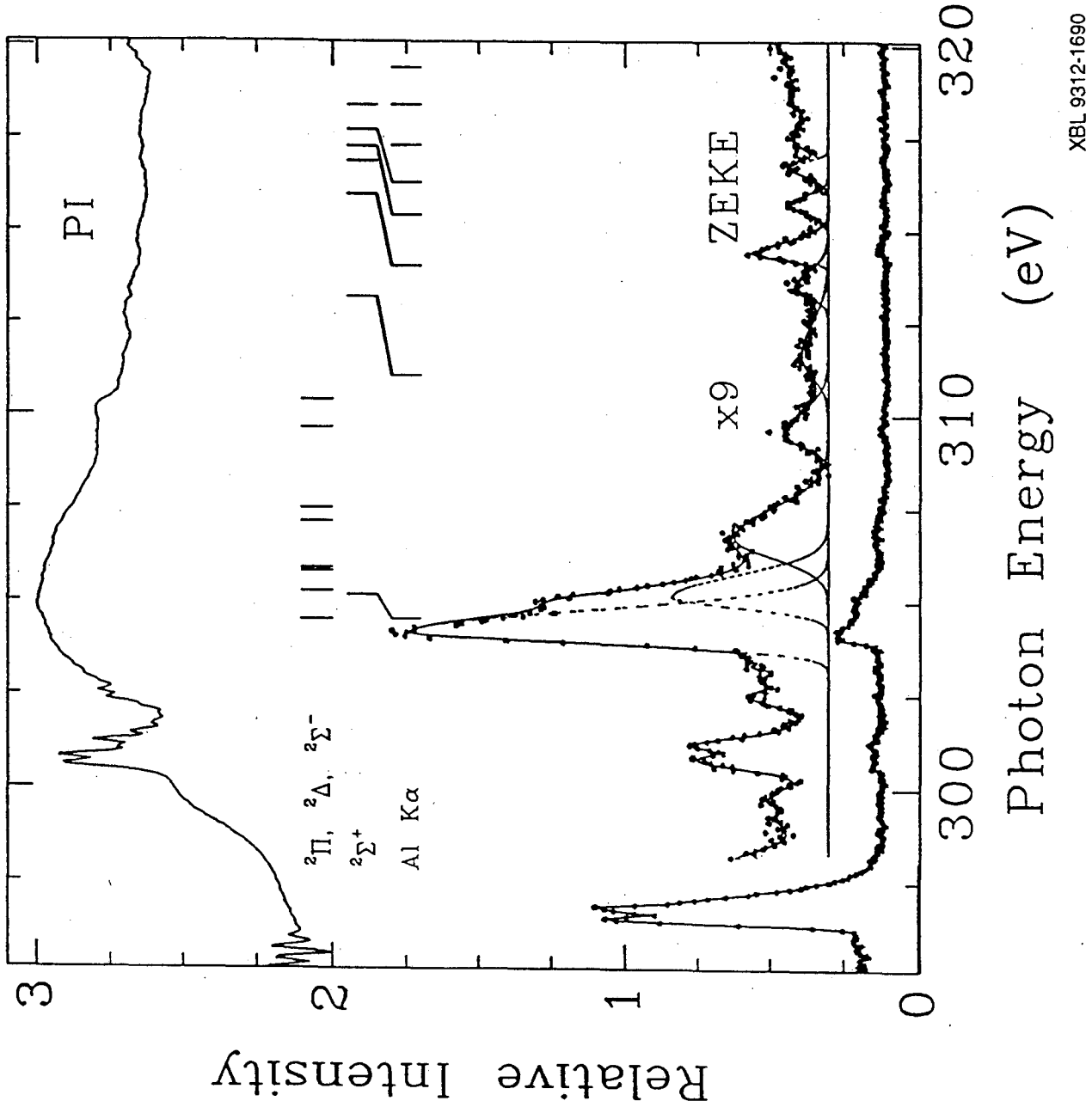
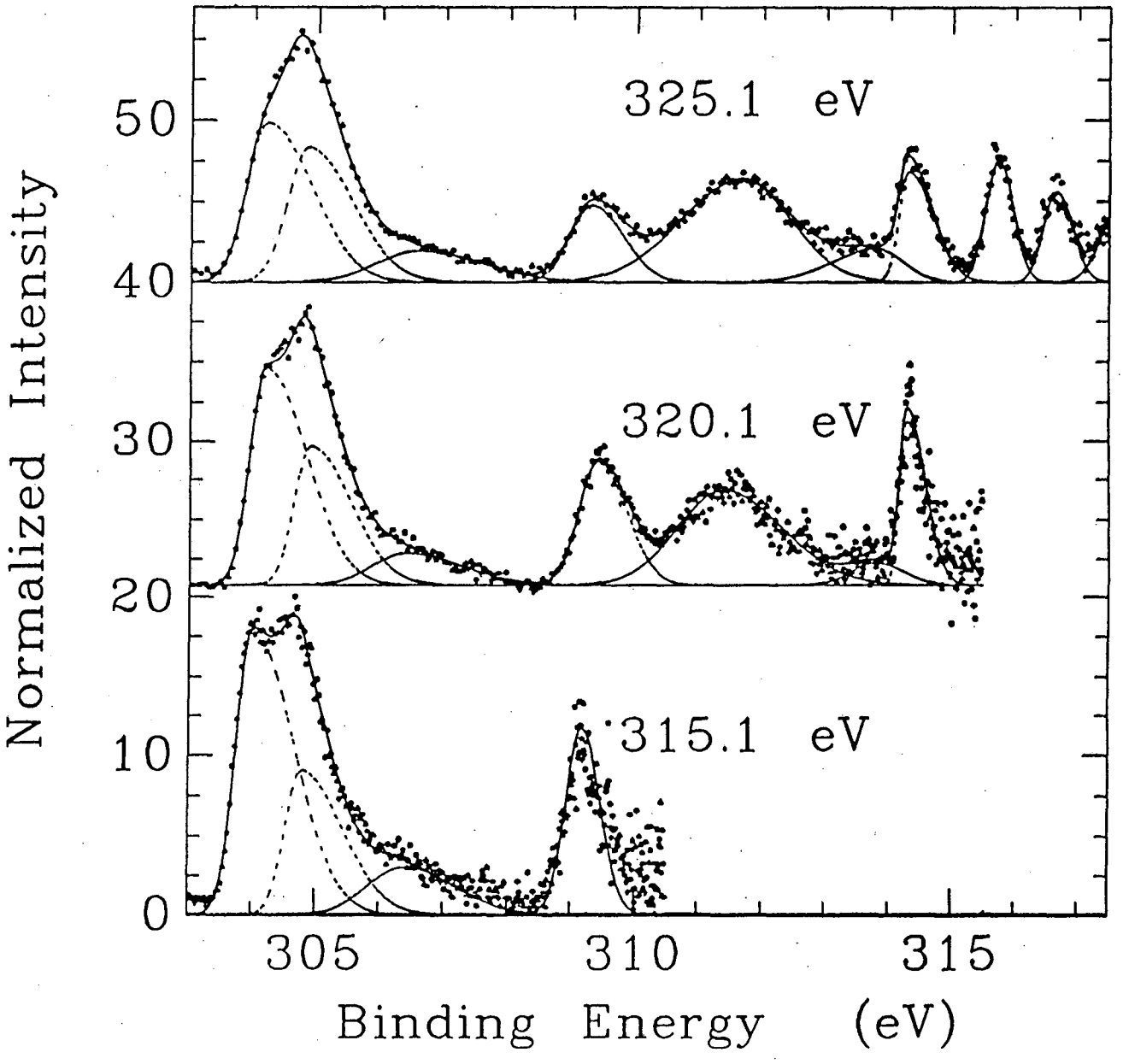

PI
$^2\Pi$, $^2\Delta$, $^2\Sigma^-$
$^2\Sigma^+$
Al Kα
x9
ZEKE
Relative Intensity
Photon Energy (eV)
0
1
2
3
300
310
320
XBL 9312-1690

Figure 1.



XBL 9312-1691

Figure 2.

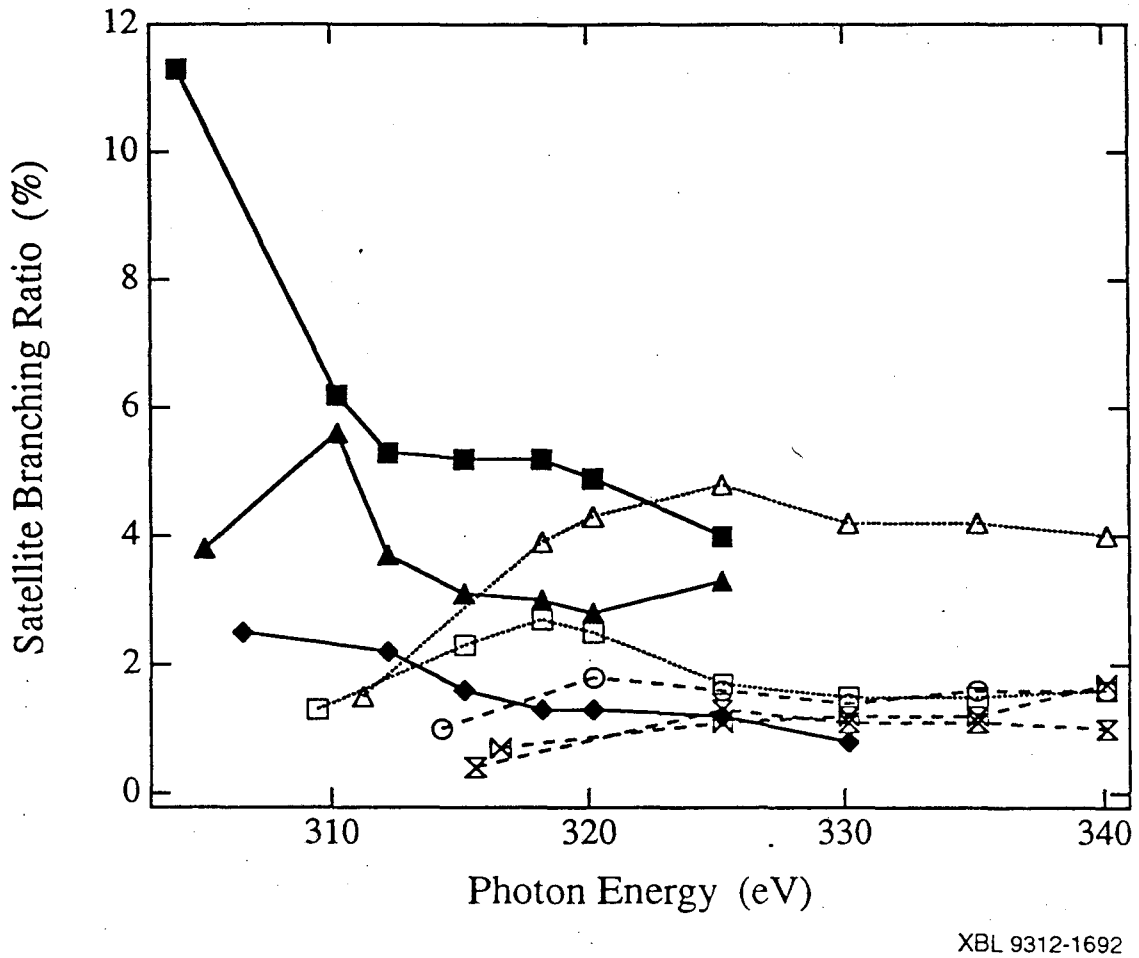

Satellite Branching Ratio (%)
12
10
8
6
4
2
0
310
320
330
340
Photon Energy (eV)
XBL 9312-1692

Figure 3.

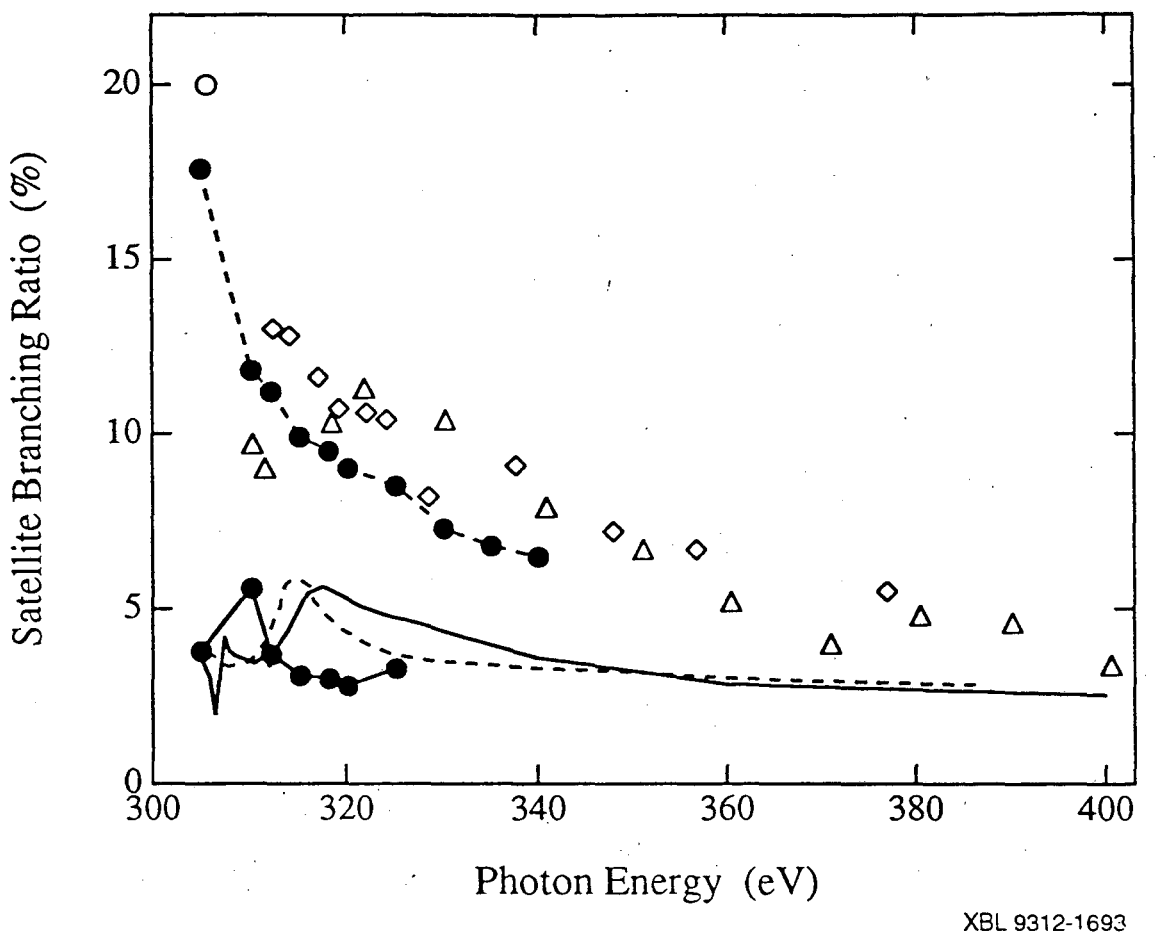

Satellite Branching Ratio (%)
20
15
10
5
0
300
320
340
360
380
400
Photon Energy (eV)
XBL 9312-1693

Figure 4.

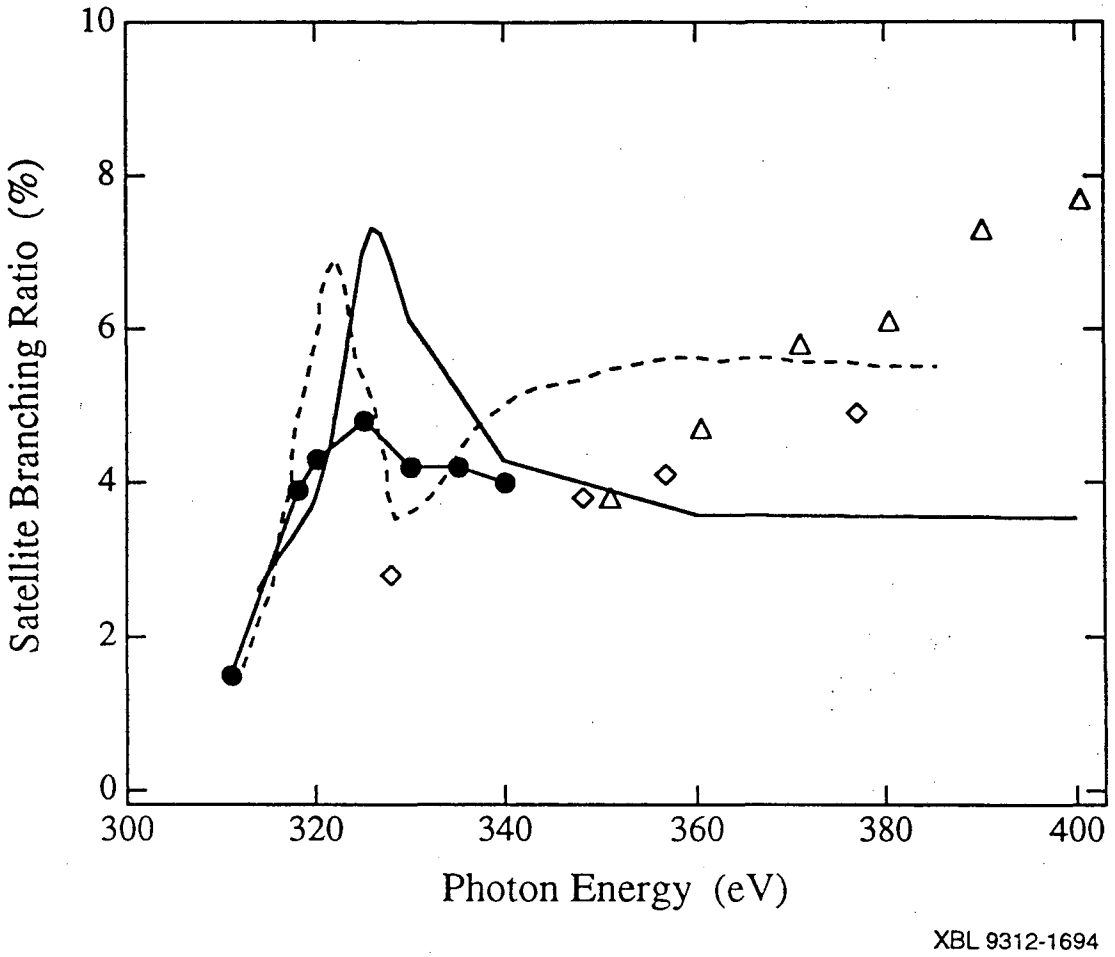
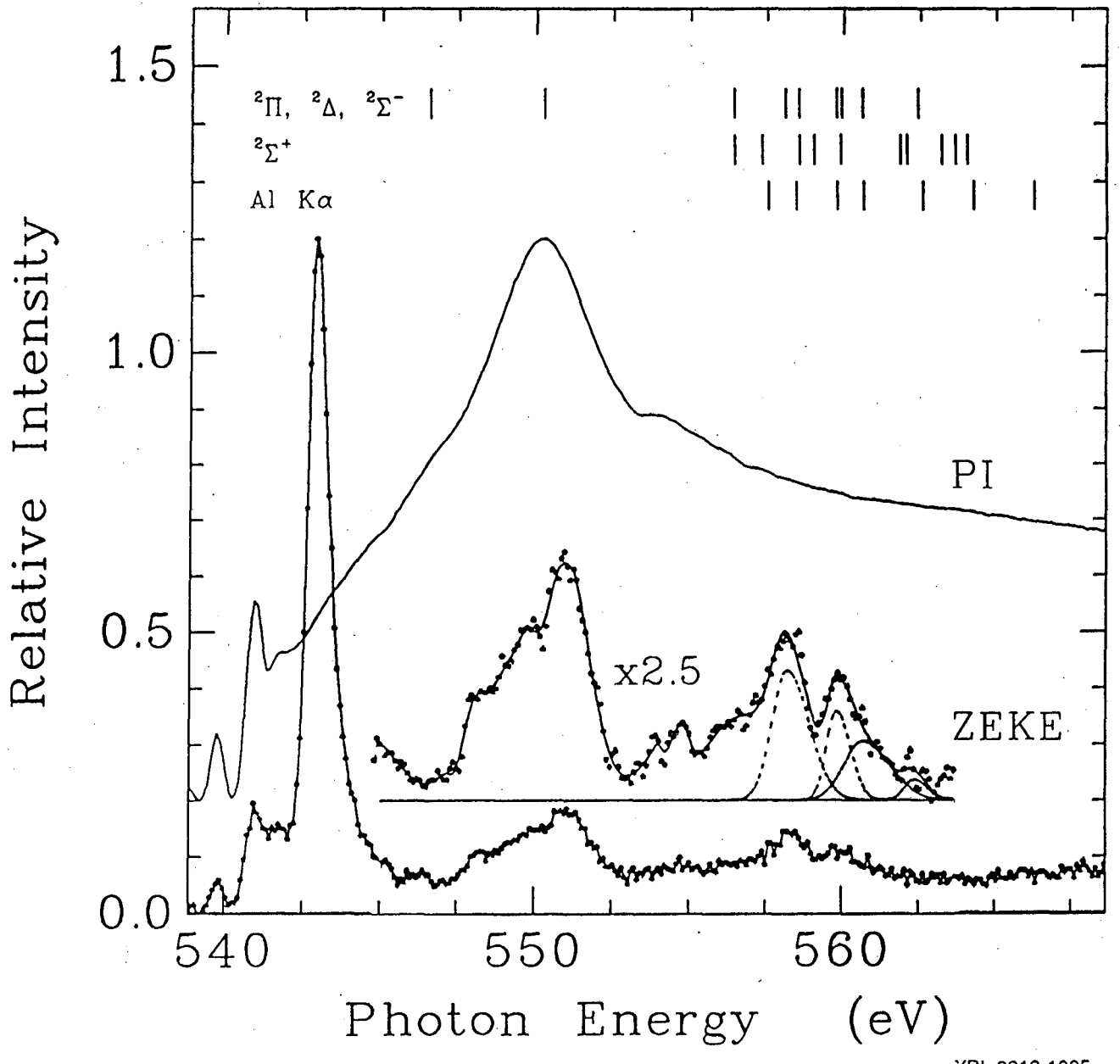

10
8
6
4
2
0
300
320
340
360
380
400
Satellite Branching Ratio (%)
Photon Energy (eV)
XBL 9312-1694

Figure 5.



XBL 9312-1695

Figure 6.

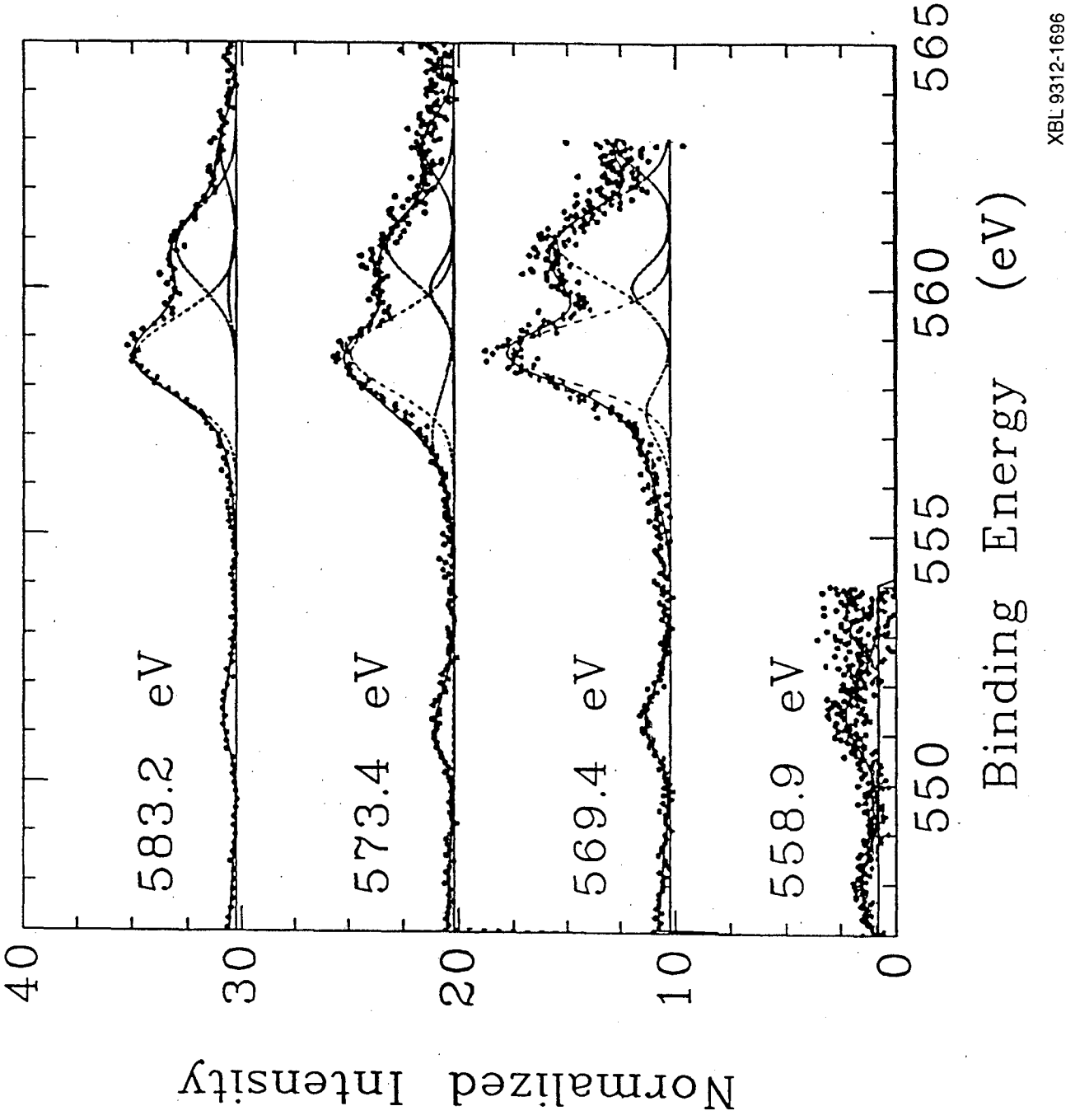

583.2 eV
573.4 eV
569.4 eV
558.9 eV
Normalized Intensity
Binding Energy (eV)
0
10
20
30
40
550
555
560
565
XBL 9312-1696

Figure 7.

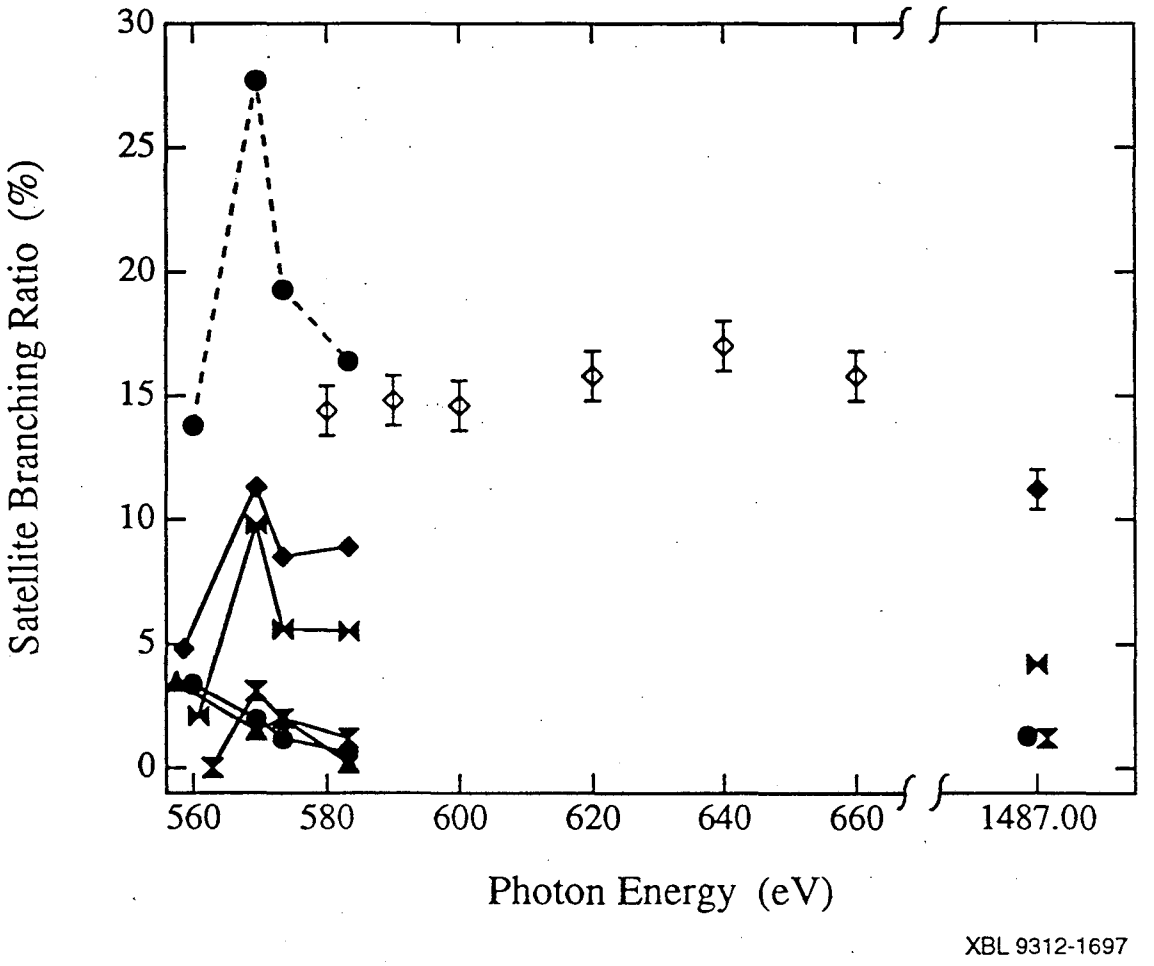

Satellite Branching Ratio (%)
30
25
20
15
10
5
0
560
580
600
620
640
660
1487.00
Photon Energy (eV)
XBL 9312-1697

Figure 8.

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