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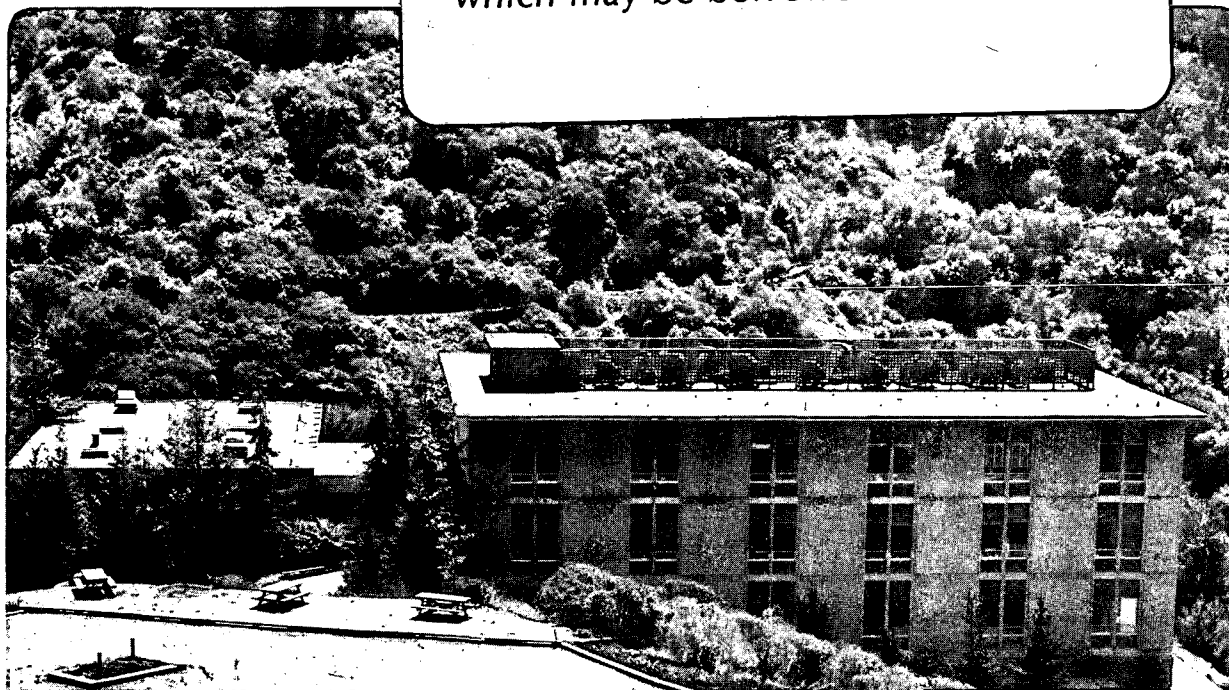
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RESONANT PROCESSES ABOVE THE CARBON 1s IONIZATION
THRESHOLD IN BENZENE AND ETHYLENE

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Resonant photoemission has been studied above the carbon 1s ionization thresholds in gas-phase benzene and ethylene. The experimental data for both molecules include relative partial cross-section and asymmetry-parameter measurements for the C 1s main line and asymmetry-parameter measurements for one C 1s shake-up satellite in each system. Resonances above the C K edge have been analyzed on the basis of their decay to either the C 1s main-line or valence-hole states, and have been tentatively assigned as either shape resonances or doubly excited states according to their observed one-electron or many-electron decay, respectively. The importance of determining the resonant behavior of all available photoemission channels in the proximity of a resonance is thus illustrated.

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I. INTRODUCTION

In simple hydrocarbons such as C_2H_4 , C_2H_2 , and C_6H_6 , the absorption spectra in the photon-energy range 280–320 eV, which includes the carbon 1s ionization thresholds, are very rich in structure both below and above the K edge.^{1,2} To illustrate, Fig. 1 contains electron energy-loss spectra, which simulate photoabsorption spectra under appropriate conditions,¹ around the carbon K edges of C_6H_6 and C_2H_4 .² In benzene, the C 1s ionization threshold is at 290.2 eV. Below threshold, the absorption spectrum shows an intense peak at 285.2 eV, followed by weaker features converging to the K edge. Above threshold, there is an intense and relatively sharp feature at 293.5 eV and another broader feature peaking near 300 eV. In ethylene, the C 1s threshold is at 290.6 eV. Below threshold, there is one intense peak at 284.7 eV, followed by a series of weaker structures converging to the K edge, as in benzene. Above threshold, there are two small peaks at 292.2 and 295.6 eV, followed by a broad weaker structure at ~300 eV.

There is general agreement in the literature about the nature of the most intense sub-threshold absorption features in these two molecules.² These peaks signify excitation to discrete states; either unoccupied molecular orbitals (near 285 eV), or Rydberg states closer to threshold. For both benzene and ethylene, the most intense peak below threshold corresponds to a transition from the C 1s core level to the lowest unoccupied π^* molecular orbital. The weaker sub-threshold features at higher energies have been assigned, in ethylene, to transitions from the C 1s levels to Rydberg orbitals, and in benzene, to a second C 1s $\rightarrow \pi^*$ transition, plus Rydberg excitations.²

The situation is more complicated for the above-threshold absorption features, which can originate from two very different resonant processes, or possibly nonresonant variations of the cross section. In general, the resonant phenomena giving rise to above-threshold maxima in the total absorption cross section fall into two main categories; shape resonances and autoionizing doubly excited states. A shape resonance is considered to be a single-channel final-state effect

in which a photoelectron is initially trapped in a quasibound state by a centrifugal barrier in the molecular potential, through which it tunnels into the continuum with an enhanced photoionization cross section and a perturbed angular distribution.³ An autoionization resonance corresponds to a multi-electron discrete transition to an excited state which decays by the ejection of an electron. Because autoionization is a many-electron process, it typically can decay into several photoemission channels, causing oscillations in the photoionization cross sections and angular distributions of each channel. A more detailed discussion of above-threshold resonant processes can be found in Ref. 4.

The nature of above-threshold resonant features cannot be determined with certainty from an absorption spectrum alone. Because only the total absorption cross section is obtained by EELS or photoabsorption measurements, the possible contributions to the resonant behavior from individual photoionization channels cannot be assessed. Analysis of the behavior of specific exit channels requires measurement of the photoemission cross section of the lines corresponding to the available photoionization channels. If the photoionization cross section is measured for all the lines in a photoelectron spectrum in the photon-energy range of a resonance, the one-electron or many-electron decay characteristics so derived can facilitate assignment as either a shape resonance or an autoionizing state.

With this thesis in mind, we report here a resonant photoemission study, based on angle-resolved time-of-flight (TOF) electron spectroscopy, of the C 1s core levels in benzene and ethylene. This is the first such study of the above-threshold resonant behavior for the C 1s core level in gas-phase hydrocarbons. For both molecules, measurements of the relative partial photoionization cross section σ and the angular-distribution parameter β were performed for the C 1s main line in the near-threshold region. The β parameter was also measured for C 1s satellites with binding energies (E_B) of 297(1) eV in C₆H₆ and 298(1) eV in C₂H₄. To analyze the resonant decay behavior of all the open channels, photoionization cross sections of the unresolved valence and C(KVV) Auger lines in the same photon-energy range were also

obtained. From these data, we observe that the absorption features at ~ 300 eV in both molecules decay only to the C 1s main line, while the features at 293.5 eV (C_6H_6) and 295.2 eV (C_2H_4) decay primarily to valence-hole states. Therefore, we tentatively assign the features at ~ 300 eV as shape resonances, while the other features at 293.5 eV and 295.2 eV are probably doubly excited discrete states.

To confirm the assignment of resonances in both molecules, theoretical calculations are still needed. Multiple scattering MS-X α calculations for benzene point to the existence of shape resonances in the outer- and inner-valence states, which may show up in the C 1s main line as well.⁵ Other MS-X α calculations for benzene⁶ attributed all the above-threshold maxima in the core-level absorption coefficient to shape resonances, at variance with the present results. The present experimental findings indicate that the resonance at 293.5 eV in C_6H_6 is not decaying strongly to the C 1s main line, and therefore is unlikely to be a shape resonance.

II. EXPERIMENTAL

Synchrotron radiation from a "grasshopper" monochromator on Beamline III-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) photoionized an effusive jet of C_6H_6 or C_2H_4 . Photoelectrons and Auger electrons were detected simultaneously at two angles, $\theta = 0^\circ$ and $\theta = 54.7^\circ$, relative to the photon polarization direction, using the double-angle time-of-flight (TOF) technique.⁷⁻⁹ For a randomly oriented sample ionized with linearly polarized light, the differential cross section can be obtained on the basis of Yang's theorem.¹⁰ At $\theta = 54.7^\circ$ ("magic angle"), the partial cross section $\sigma(h\nu)$ can be measured directly as a function of photon energy.

The asymmetry parameter β is determined from the ratio of intensities at 0° and 54.7° , correcting for the relative efficiency of the two analyzers.^{8,9} Calibration of the analyzers was done using the Ne 2s and 2p photoemission peaks, for which $\sigma(h\nu)$ and $\beta(h\nu)$ are known.¹¹ We estimate that systematic errors (not represented by the statistical error bars in our plots) are less than 10 percent for $\sigma(h\nu)$ and less than ± 0.10 for $\beta(h\nu)$.

A 1000-Å-thick silicon window separated the sample-chamber pressure (10^{-4} torr) from the monochromator vacuum (10^{-10} torr). Photoelectron spectra were taken in the photon-energy range 293.5–361 eV using a 1200 l/mm holographically ruled grating. The monochromator resolution varied from 2.0 to 3.5 eV over this range. Energy calibration of the monochromator was determined from the position of the $1s \rightarrow \pi^*$ resonances at 285.2 eV in C_6H_6 and 284.7 eV in C_2H_4 .² The sample pressure was monitored with a capacitance manometer and the photon intensity by a sodium salicylate scintillator with an optical photomultiplier tube (RCA 8850). Corrections have been made in the measured cross section for the varying response of sodium salicylate in our system over the photon-energy range in this study.¹²

III. RESULTS AND DISCUSSION

A. Partial Cross Sections

In Figs. 2 and 3 we show TOF spectra of C_6H_6 and C_2H_4 taken for 1000 sec at $\theta = 54.7^\circ$ and $h\nu = 320$ eV. The spectra show the C 1s main lines [$E_B = 290.2$ eV (C_6H_6), 290.6 eV (C_2H_4)], satellite peaks [$E_B = 297(1)$ eV (C_6H_6), 298(1) eV (C_2H_4)], and high kinetic energy peaks which include the valence and C(KVV) Auger peaks unresolved due to the poor resolution of TOF analysis of fast electrons.

Figure 4 shows the photoionization cross section for the C 1s main line in benzene over the photon-energy range 293.5–340 eV. There is a broad maximum in the cross section around 298(1) eV, in near coincidence with the second resonance in the absorption cross section at ~ 300 eV. To lower energies, we could only measure the cross section of the C 1s main line down to 293.5 eV photon energy, or 3.3 eV above threshold, because of the ~ 2 eV bandwidth of the incident synchrotron radiation. Therefore, only the high-energy side of the 293.5 eV resonance in benzene would be included in the present measurements. Nevertheless, we observe a decrease in the C 1s cross section to lower energy which does not indicate any obvious resonant behavior, at least not to the extent present in the total cross section.

In Fig. 5, we show the cross section for the C 1s main line in ethylene. There is an enhancement evident, with a maximum at 300(1) eV, which probably is related to the corresponding feature in the absorption coefficient at ~300 eV. Below 300 eV, the cross section decreases, with no evident counterpart to the maximum in the absorption coefficient at 295.2 eV, although our lower resolution would preclude sharp structure. Here, too, as in benzene, the C 1s cross-section measurements were restricted to $h\nu \geq 295$ eV because of the large photon-energy bandwidth, thus including only the high-energy side of the 295.2 eV absorption feature.

To gain more information on the decay patterns of the above-threshold resonances, we measured the partial photoionization cross section for the high-kinetic-energy peak, which includes both C(KVV) Auger and valence electrons. The cross section of this peak itself is not sensitive to different decay channels and roughly follows the behavior of the C 1s main-line cross section. However, the $(\text{C(KVV) Auger-plus-valence})/(\text{C 1s})$ branching ratio (R) is more informative. Ignoring shake-off and core-level shake-up (which are unimportant within 10 eV above the K edge), resonant processes involving only the C 1s main line should give rise to a flat R; the C(KVV) Auger intensity will mimic the C 1s intensity, and the valence contribution will provide an essentially constant background (the presence of this background will cause R to be greater than unity, however). Conversely, if channels other than the C 1s main line are enhanced on resonance, R will vary with photon energy, because these other channels will add to the Auger-plus-valence peak but not to the 1s main-line peak. In some sense, the high-kinetic-energy peak represents a total-yield measurement, which can be used to experimentally compare the C 1s main-line cross section to the total absorption cross section.

The measured values of R for benzene and ethylene are shown in Figs. 6 and 7, respectively, illustrating nonconstant behavior at most energies. These data require some explanation; so we will begin near threshold and work to higher energies. The following discussion applies to both molecules, unless stated otherwise.

Below ~296 eV, R increases dramatically towards threshold, whereas the C 1s cross sections (Figs. 4 and 5) are constant or decreasing in the same energy range. We interpret these observations to mean that channels other than the C 1s main lines are resonantly enhanced at the 293.5-eV (C_6H_6) and 295.2-eV (C_2H_4) features, indicating the importance of multi-electron decay. These other channels must be valence-hole states, based on energy conservation alone.

Between 296 eV and 305 eV, the roughly constant R indicates that no channels other than C 1s are strongly enhanced at the ~300-eV resonance. This observation, along with the large enhancement of the C 1s cross section at 300 eV (Figs. 4 and 5), indicates that primarily or only the C 1s main-line channel is experiencing this resonance. This conclusion is complicated somewhat for benzene because of the "bump" in R near 300 eV.

However, we can attribute this behavior at ~300 eV to the onset of a multi-electron satellite continuum, which adds to the C(KVV) Auger intensity but, of course, not to the C 1s main-line intensity. The satellites in question are visible in the TOF spectra of Figs. 2 and 3. Further studies of these satellites' relative intensity in this energy range would be very useful.

The increasing R at photon energies above ~305 eV is probably due to an increasing contribution of satellites and shakeoff to σ (total). There are Auger electrons from the decay of the satellites visible in Figs. 2 and 3, and possibly other low-intensity satellites at higher E_B , and from multiple-ionization processes at higher photon energies followed by Auger decay. This tends to produce an increasing (Auger-plus-valence)/(C 1s) ratio at higher energy.

We conclude that the resonances which exhibit different decay patterns have a very different nature. We tentatively assign the resonant processes at ~300 eV as shape resonances in both molecules, since we have deduced from our data that they apparently have single-channel decay character. The lower-energy resonances at 293.5 eV (C_6H_6) and 295.2 eV (C_2H_4) are probably not core-level shape resonances, because they decay into channels other than the C 1s main line. We tentatively assign them as doubly excited states which can autoionize to valence-hole configurations, and can make some tentative statements about possible doubly

excited states in this energy range. The C 1s $\rightarrow \pi^*$ discrete transition takes place ~ 5 eV below the C 1s threshold. The lower-energy resonances in both molecules lie ~ 4 eV below the ionization threshold of respective satellites. The doubly excited states would have the generalized configuration $1s^{-1}val^{-1}\pi^*(\pi)^*$. Such an excited state will probably decay through autoionization to states with configurations $val^{-1}(val')^{-1}\pi^*$, which correspond to valence correlation satellites.

The present results should be tested both by higher-resolution experimental studies and by calculated partial cross sections to provide a theoretical framework for assigning the resonances described above. In fact, some related theoretical results on resonances in benzene are available.^{5,6} The measured σ and β values for the outer- and inner-valence levels of benzene have been compared to multiple-scattering MS-X α calculations.⁵ Shape resonances were predicted theoretically and confirmed experimentally in the majority of the valence levels. Therefore, shape resonances are expected in the K-shell as well. However, these particular theoretical calculations have not yet been extended to the C 1s shell.

Another set of theoretical and experimental data on resonant processes in benzene has been reported⁶ in which near-edge x-ray absorption fine structure (NEXAFS) data for benzene molecules adsorbed on the platinum(111) surface were compared to gas-phase total absorption measurements obtained by EELS, and to MS-X α theoretical results. In the NEXAFS data on chemisorbed benzene, the two resonances above the carbon K edge were found to have the same polarization dependence, corresponding to excited states with σ symmetry; i.e., parallel to the molecular plane. The sub-threshold resonance at 285.2 eV showed a polarization dependence typical of a final state with π symmetry, as expected. The MS-X α calculations of Ref. 6 assigned both above-threshold resonances as shape resonances (actually three shape resonances were predicted). However, from the present results it is suggested that the two above-threshold resonances have different natures, and in particular that the resonance at 293.5 eV is most likely not a core-level shape resonance. We have no definite explanation for this

discrepancy, but we note that there need not be a one-to-one correspondence between the number and positions of experimentally observed shape resonances and the MS-X α model predictions (see, e.g., SiCl₄).¹³ Thus, the three shape resonances in C₆H₆ predicted above the C 1s threshold may produce only one maximum at 300 eV in the absorption coefficient, and the polarization dependence measured by NEXAFS may not be definitive in the assignment of above-threshold features as shape resonances.

There also exists previous experimental and theoretical work on resonant processes in ethylene in which NEXAFS data for ethylene chemisorbed on platinum(111) are compared to MS-X α calculations.¹⁴ The NEXAFS data show one above-threshold resonance with σ symmetry at 293 eV, assigned as a shape resonance by the MS-X α results. But there are three resonances in the gas-phase absorption cross section, at least one of which appears to have different decay characteristics. It is not clear why only one resonance is visible in the NEXAFS spectrum, or which of the three resonances apparent in the gas-phase absorption coefficient has the single NEXAFS feature as a counterpart. Therefore, the assignment of a shape resonance from the NEXAFS data solely on the grounds of polarization dependence appears not to be straightforward.

B. Angular Distributions

In Figs. 8 and 9 we show $\beta(h\nu)$ for the C 1s main lines in benzene and ethylene, respectively. The resonant behavior clearly apparent in $\sigma(h\nu)$ has no evident counterpart in the β curves. The data show a smooth increase of β with increasing photon energy, tending toward the asymptotic value of 2 expected for levels with s atomic character. There are no clear variations corresponding to the pronounced maxima in the cross section. This is at variance with other cases, in which both experimentally^{15,16} and theoretically¹⁷⁻¹⁹ it was found that a maximum in the photoionization partial cross section attributed to a shape resonance was accompanied by a corresponding oscillation in β . Theoretical calculations of the β parameter for the C 1s main lines might help clarify this experimental finding.

Also included in Figs. 8 and 9 are the angular-distribution asymmetry parameters (β) measured for the satellites shown in the photoelectron spectra of Figs. 2 and 3. The general appearance of the β trend for each satellite is similar to that for its respective main line. In fact, if we align the main-line and satellite β results according to the photoelectron kinetic energy (i.e., shift the β curve for the satellite downward ~ 7 eV), the two β curves almost coincide over the commonly measured range, up to 40 eV above threshold. This hypothesis would be consistent with the resonant state reached by the main line at a photon energy of 300 eV being a shape resonance, since the same resonant final state could be accessible for both a main line and a satellite at the same kinetic energy, and therefore at different photon energies. However, very little is known about the behavior of satellites in the region of a shape resonance, and further work is needed to confirm this hypothesis.

IV. CONCLUSIONS

For both benzene and ethylene, the two above-threshold resonances we have studied in the carbon K-edge region show different behavior. Namely, the lower-energy ones at 293.5 eV (C_6H_6) and 295.2 eV (C_2H_4) appear to decay to valence-hole states. Therefore, they have been assigned as doubly excited states decaying by autoionization. This assignment disagrees with a previous interpretation.⁶ The higher-energy resonances at ~ 300 eV appear to have one-electron nature, decaying only to the C 1s main-line, and have been tentatively assigned as shape resonances. In both molecules, the angular distribution for the C 1s main line and a satellite suggest analogous behavior of the two photoionization channels as functions of kinetic energy. Finally, higher-resolution measurements and more detailed theoretical calculations of cross sections and angular distributions for the C 1s main lines and satellites are needed to confirm the above assignments.

The present results for resonant processes above the carbon K edge in benzene and ethylene confirm the importance of analyzing all available photoionization channels in the proximity of a maximum in the total absorption cross section. Such differential analysis is essential in

determining the nature of the resonance, in particular its single-channel or multi-channel decay character. Information about the decay properties of a resonance is necessary, but not sufficient, in assigning it as a shape resonance or an autoionizing excited state. The same experimental evidence cannot be obtained by measuring only the total absorption cross section. Also, the symmetry of a resonance, as determined by polarization-dependence measurements, is not in itself sufficient evidence to assign a shape resonance.

ACKNOWLEDGEMENTS

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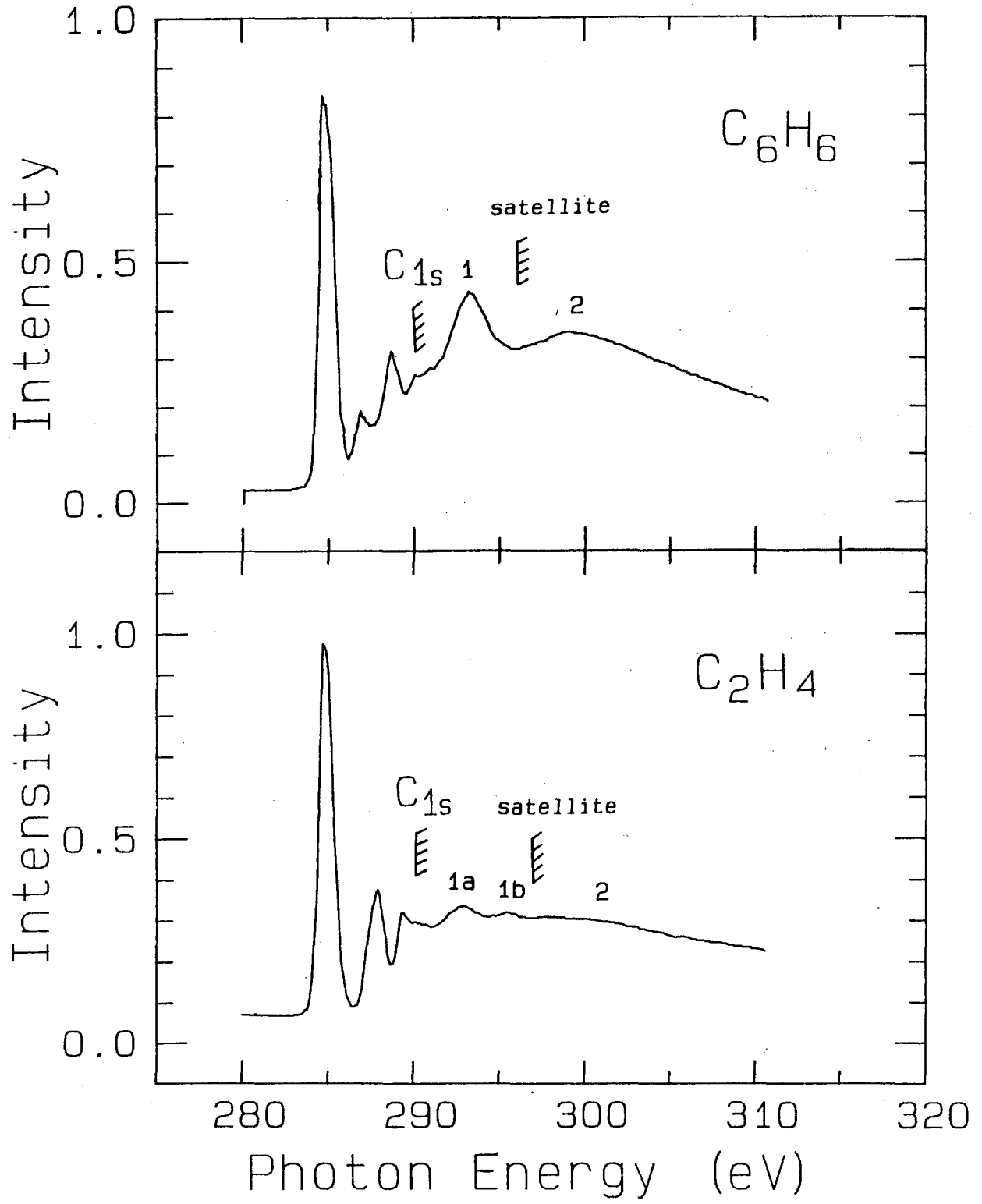
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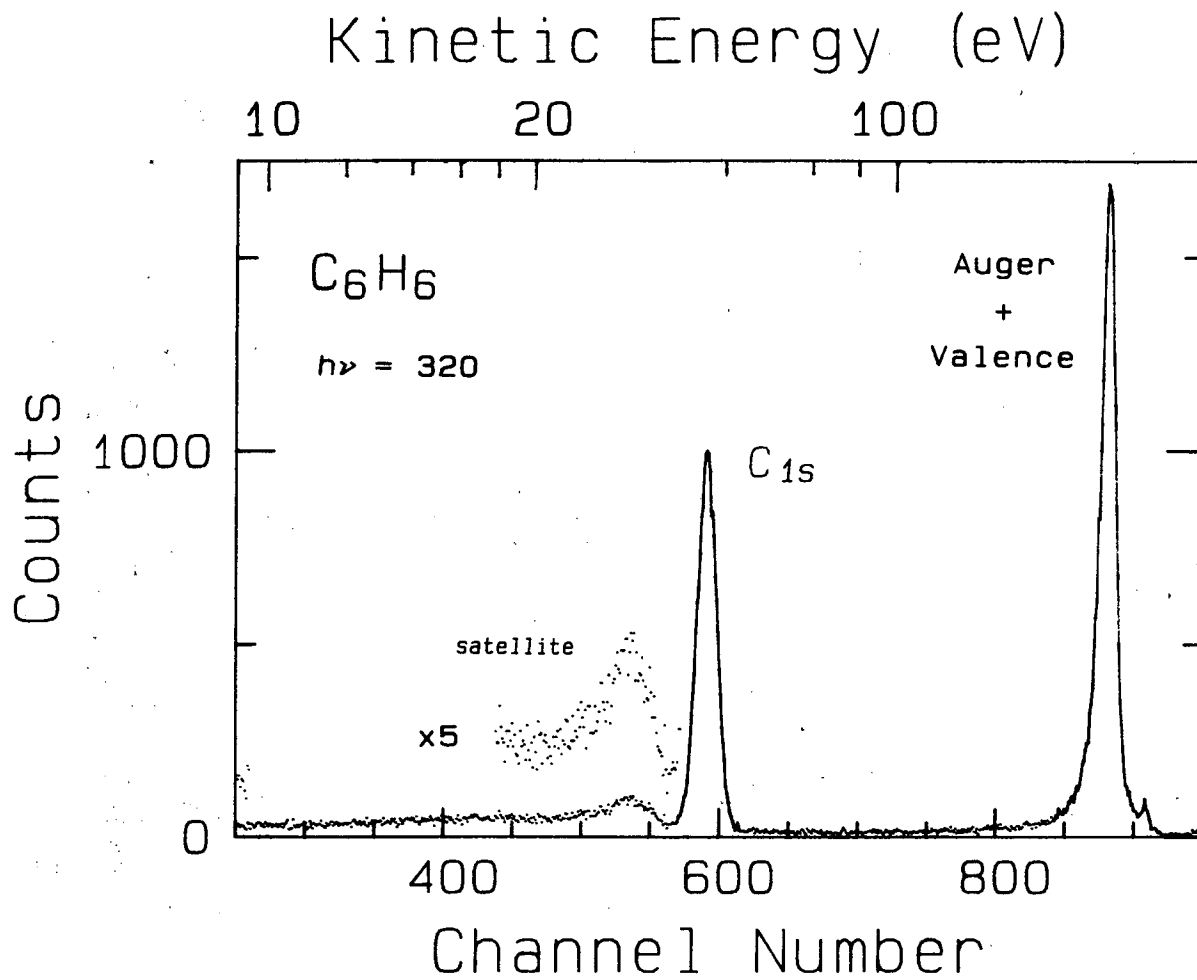
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FIGURE CAPTIONS

- Fig. 1. Total absorption cross section measured by EELS (Ref. 2) around the carbon K edge in C_6H_6 and C_2H_4 . In both cases, the ionization thresholds for the C 1s main line and a related satellite are shown by hatched marks.
- Fig. 2. TOF spectrum of benzene taken at 320 eV photon energy and $\theta = 54.7^\circ$. The binding energies of the C 1s main line and the satellite are 290.2 and 297(1) eV, respectively. The peaks at high kinetic energy include the unresolved C(KVV) Auger and valence electrons.
- Fig. 3. TOF spectrum of ethylene taken at 320 eV photon energy and $\theta = 54.7^\circ$. The binding energies of the C 1s main line and satellite are 290.6 and 298(1) eV, respectively. The peaks at high kinetic energy include the unresolved C(KVV) Auger and valence electrons.
- Fig. 4. Relative partial photoionization cross section for the C 1s main line in benzene. Statistical error bars are either shown or are smaller than the symbol size. For comparison, the EELS curve from Fig. 1 is superimposed.
- Fig. 5. Relative partial photoionization cross section for the C 1s main line in ethylene, as in Fig. 4.
- Fig. 6. Ratio of the C(KVV) Auger-plus-valence peak intensity relative to the C 1s main-line peak intensity in benzene.
- Fig. 7. Ratio of the C(KVV) Auger-plus-valence peak intensity relative to the C 1s main-line peak intensity in ethylene.
- Fig. 8. Angular-distribution parameter for the C 1s main line and the 297 eV satellite in benzene.
- Fig. 9. Angular-distribution parameter for the C 1s main line and the 298 eV satellite in ethylene.

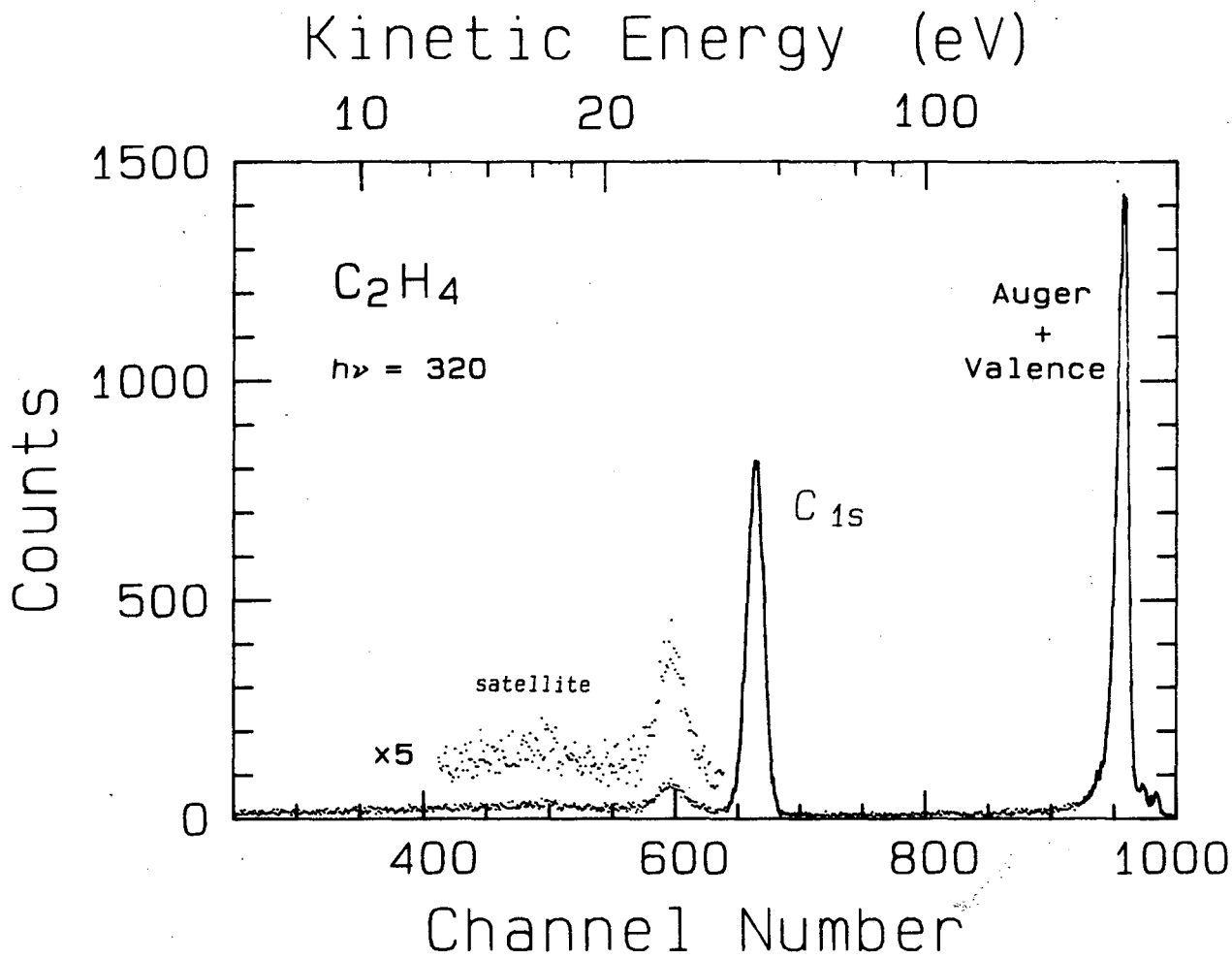


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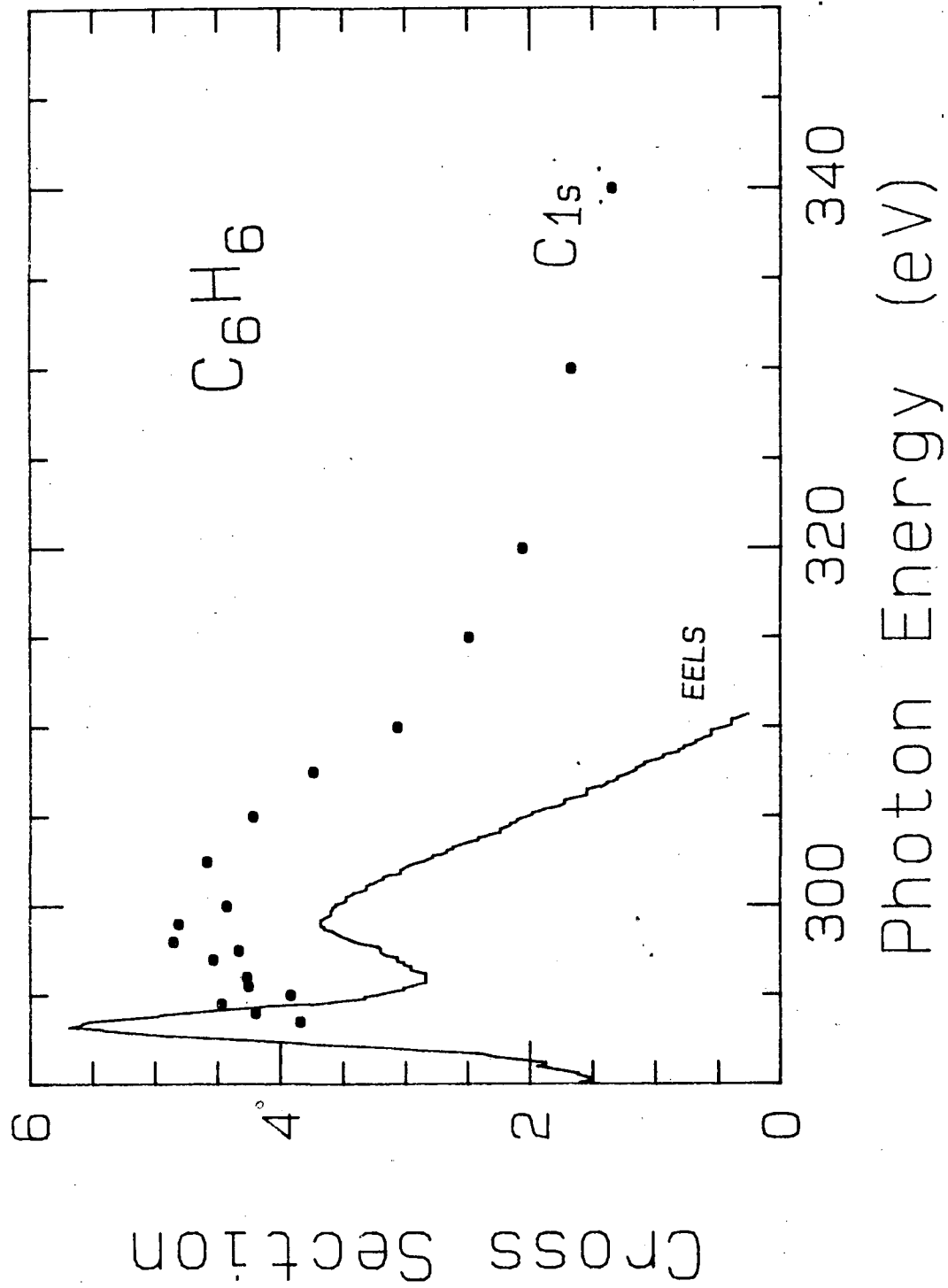
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Figure 2



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Figure 3



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Figure 4

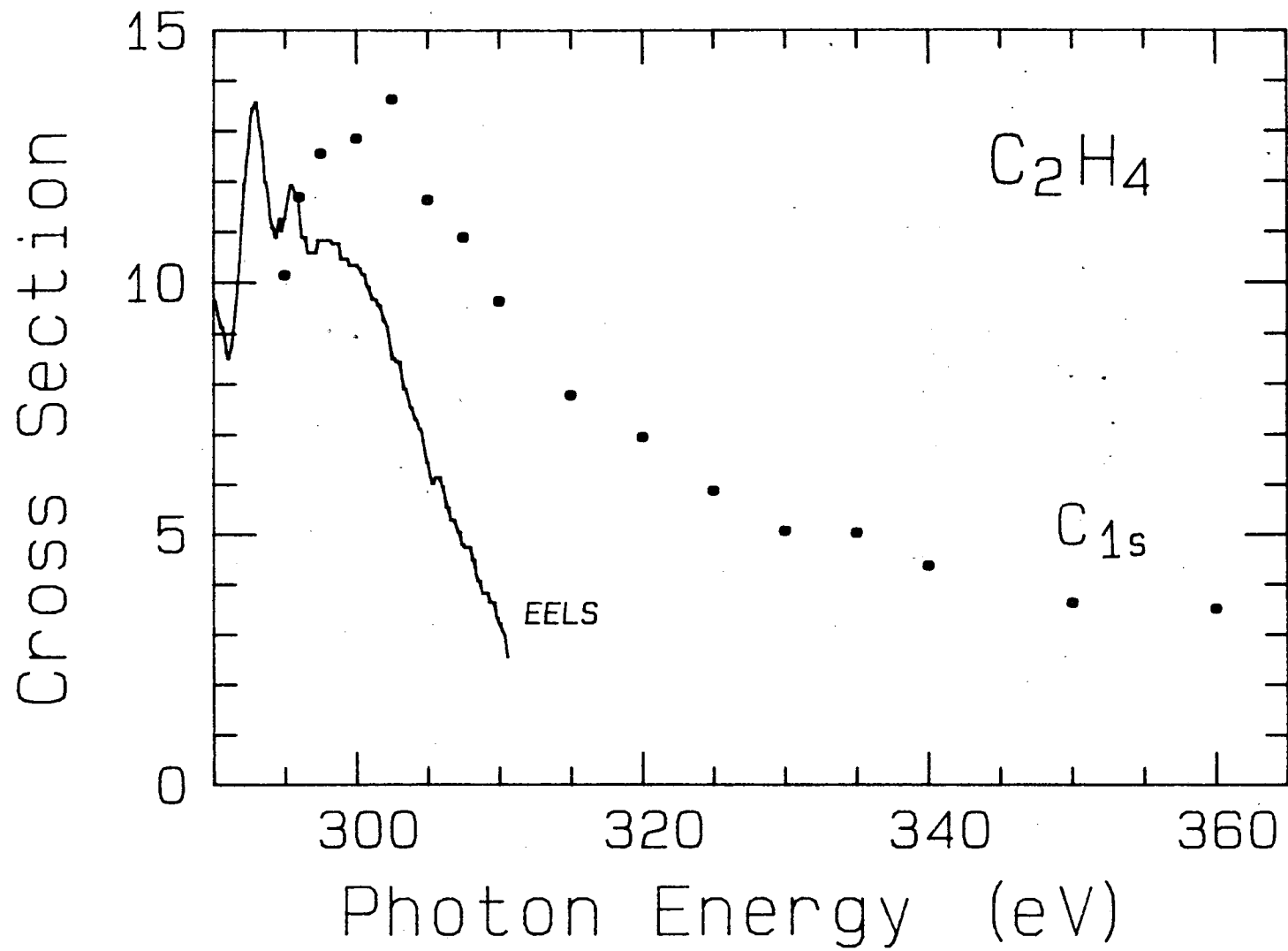


Figure 5

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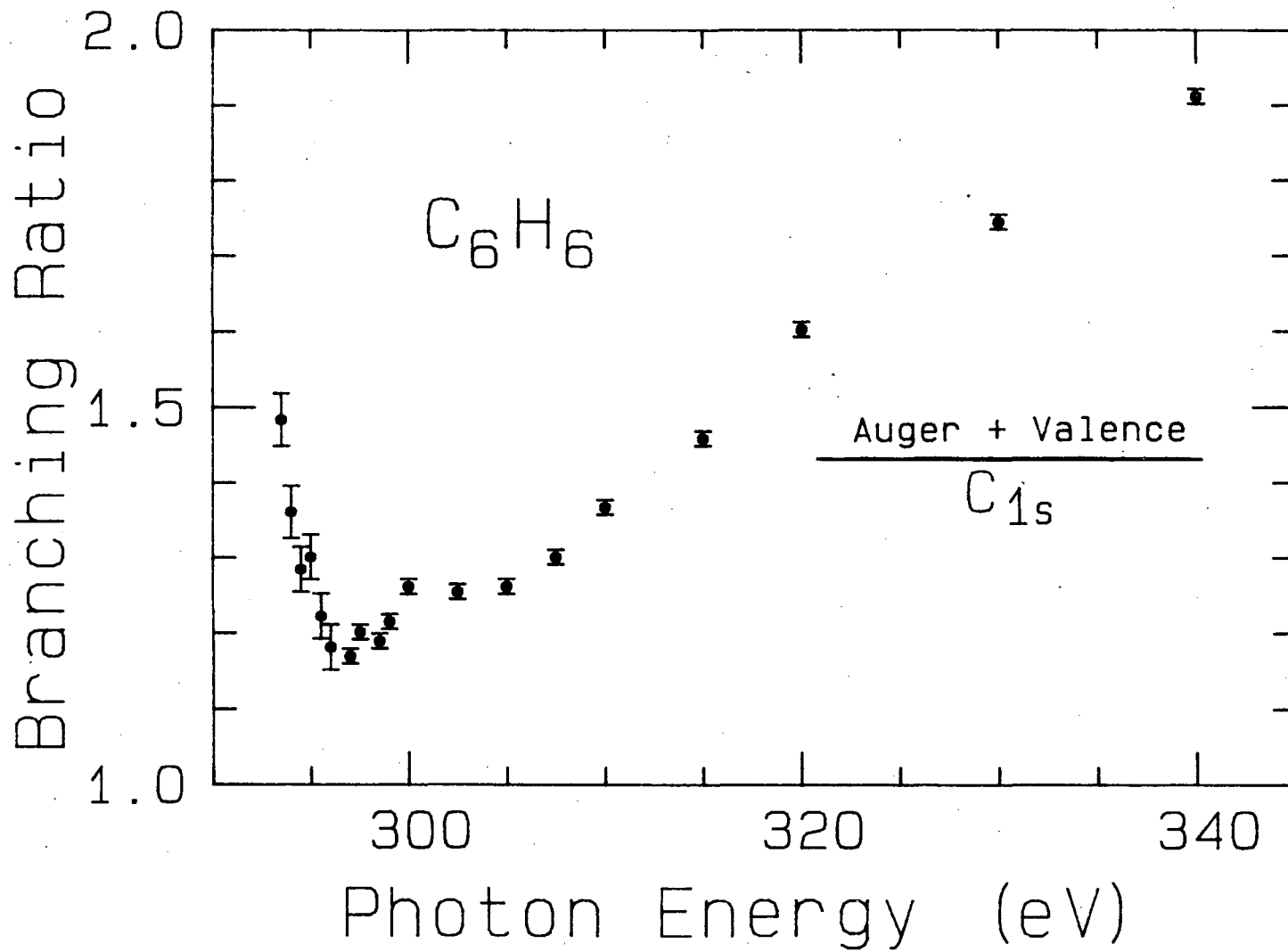
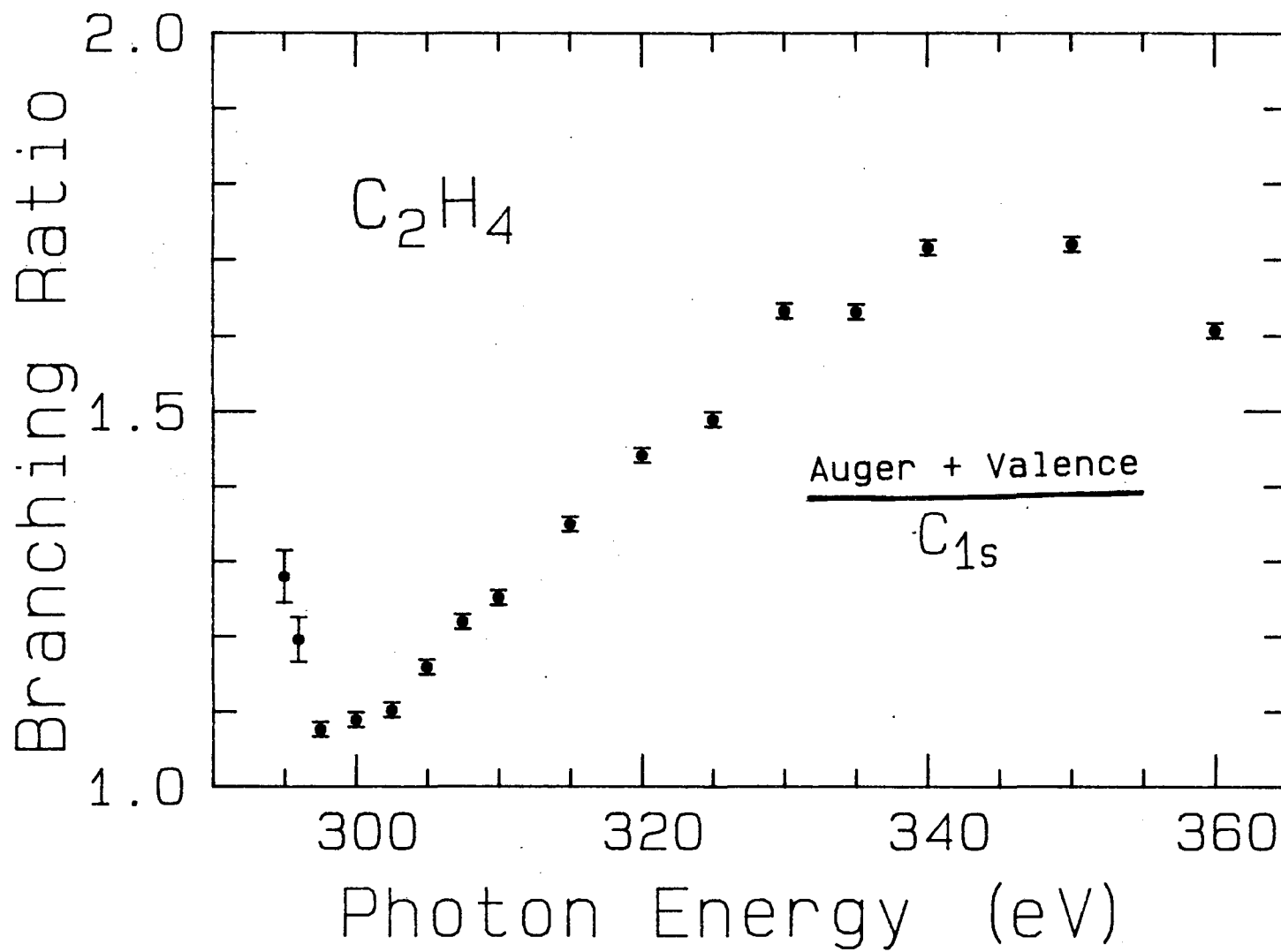


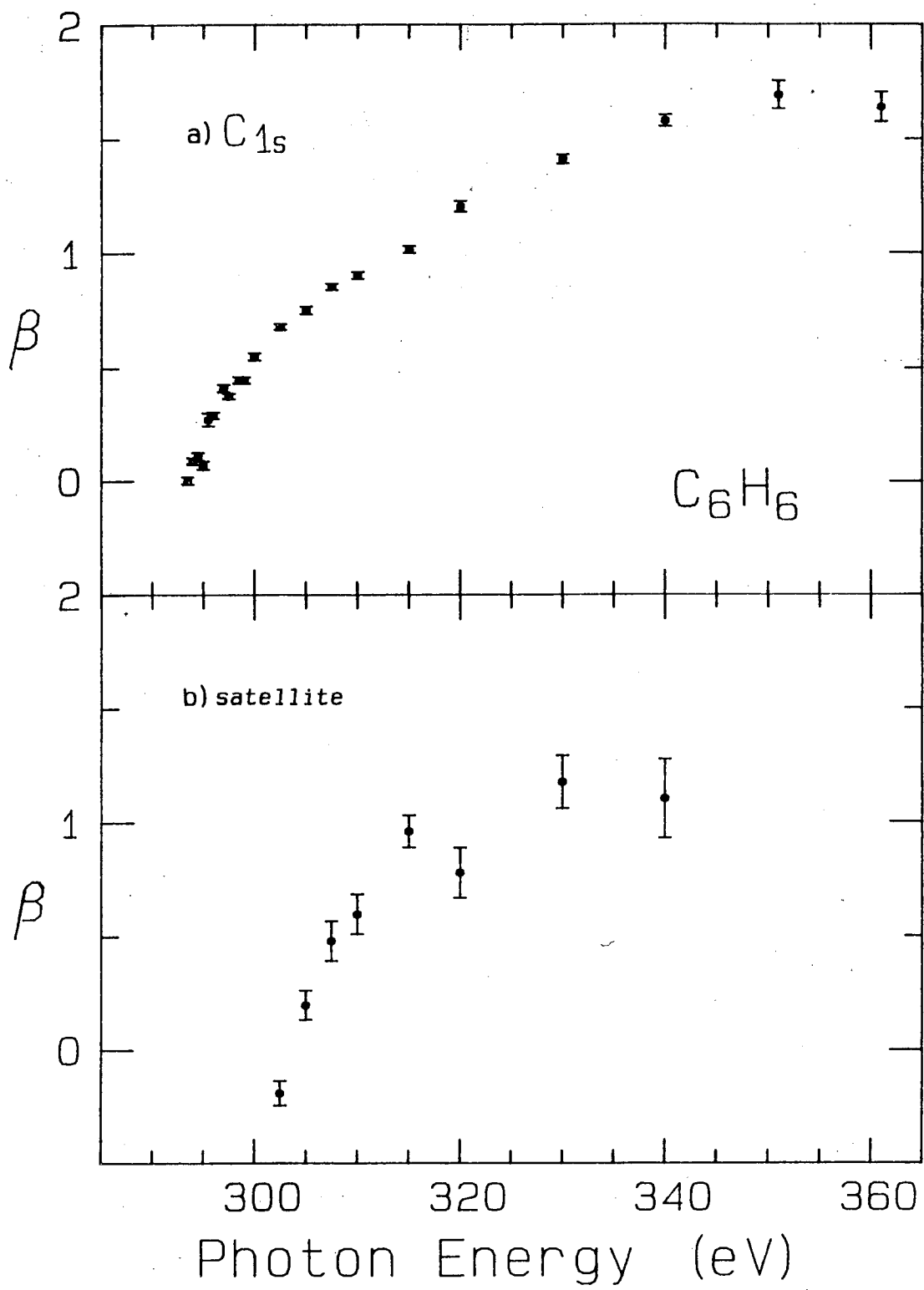
Figure 6

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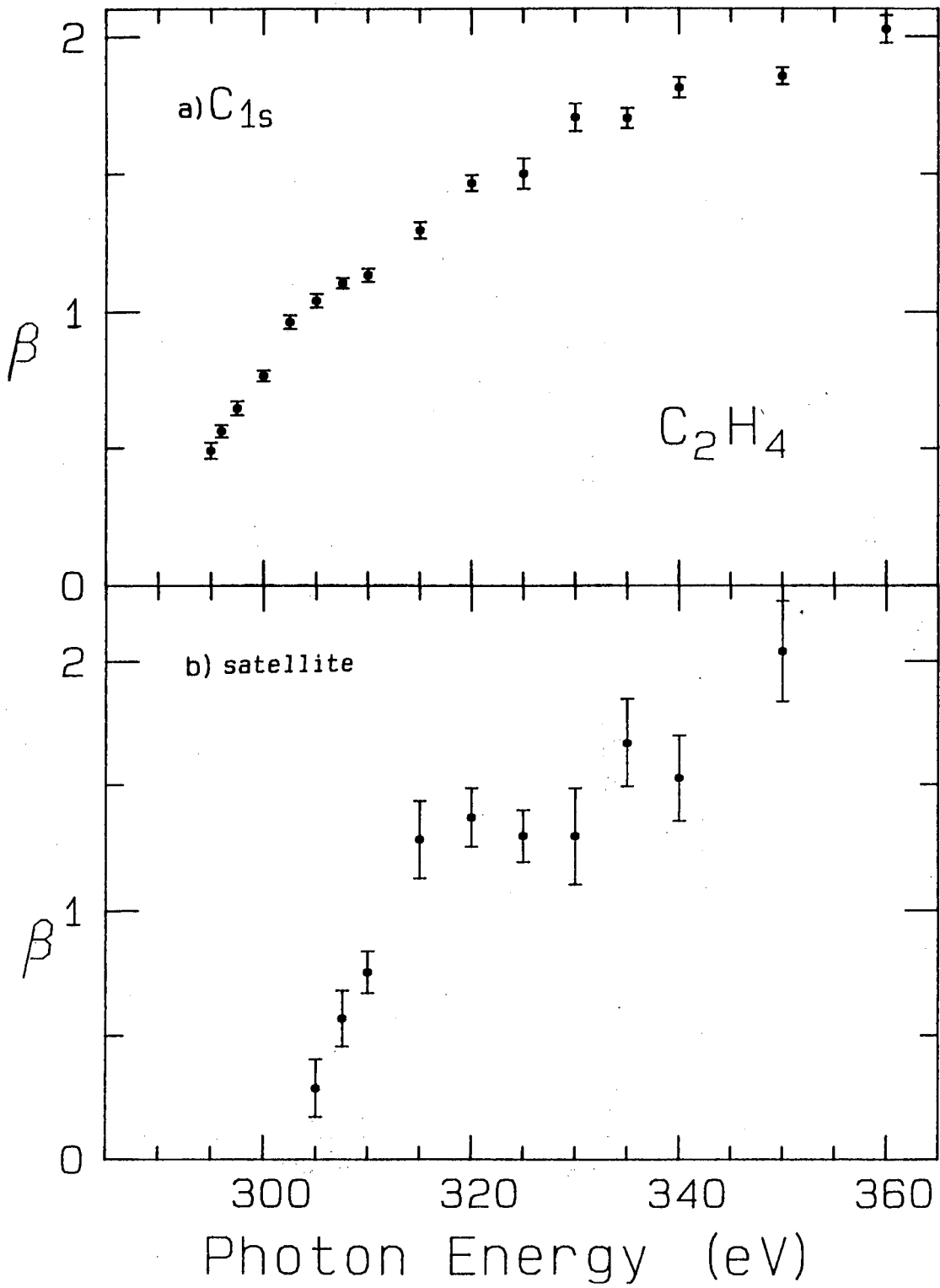
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Figure 7



XBL 885-1788

Figure 8



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Figure 9

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