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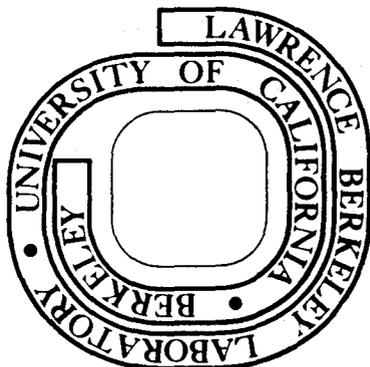
M. S. Banna and D. A. Shirley

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MOLECULAR PHOTOELECTRON SPECTROSCOPY AT 132.3 eV

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ABSTRACT: The molecular photoelectron spectra of gaseous N_2 , CO, C_2H_4 , and O_2 were obtained using yttrium M ζ x-rays (132.3 eV). Comparison with spectra taken with MgK $\alpha_{1,2}$ x-rays (1253.6 eV) showed the molecular orbitals derived from atomic 2p orbitals to be emphasized in the YM ζ spectra. Orbital compositions were confirmed in N_2 and CO, and the presence of several peaks was either better established or detected for the first time (e.g., a $^2\Pi_u$ state at 23.5 eV in O_2^+) in C_2H_4 and O_2 . The relative cross section predictions of Rabalais et al. were tested by these spectra. The theoretical values, which were based on ground-state wavefunctions and plane-wave (PW) or OPW continuum states, were found to agree qualitatively with experiment, establishing that this level of theory has diagnostic value. Quantitative agreement is lacking, however. The potential application of 132.3 eV x-rays to the study of photoemission from adsorbed molecules on surfaces is emphasized.

I. INTRODUCTION

Recent work in this laboratory^{1,2)} has dealt with the molecular orbital photoelectron spectra of a number of small molecules. It was found that orbital assignment was considerably facilitated by comparing the relative intensities obtained with $MgK\alpha_{12}$ (1253.6 eV) and $YM\zeta$ ³⁾ (132.3 eV) x-rays. The relationship between the intensity of an orbital at a certain photon energy and its atomic orbital composition was emphasized.

To determine the range of applicability of the cross section trends at 132.3 eV observed in fluoromethanes¹⁾ and the second-row hydrides,²⁾ we have undertaken a study of N_2 , CO, C_2H_4 and O_2 . The data presented here may be useful in future chemisorption studies⁴⁾ with the $YM\zeta$ source. Because of the small electron escape depth associated with 132.3 eV x-rays, electrons from the substrate would not interfere significantly with the spectrum of the adsorbed species. The $YM\zeta$ x-ray thus may well become an important tool in surface work.

We report the 132.3 eV molecular orbital spectra of N_2 , CO, C_2H_4 and O_2 , together with the 1253.6 eV spectra of C_2H_4 and O_2 . The core region of C_2H_4 is also discussed. Studies of the valence region in N_2 ,⁵⁾ CO⁵⁾ and C_2H_4 ⁶⁾ with monochromatized $AlK\alpha$ x-rays (1486.6 eV) have been conducted by the Uppsala group, who also previously reported the unfiltered $MgK\alpha_{12}$ (1253.6 eV) spectra of N_2 , CO and O_2 .⁷⁾ Theoretical photoelectric cross sections at different photon energies are also available for N_2 ,⁸⁾ CO⁸⁾ and C_2H_4 .⁸⁾

This paper is organized as follows: Section II gives a brief account of experimental procedures. The N_2 and CO spectra are discussed

together in Section III, C_2H_4 in Section IV, and O_2 in Section V. Finally, Section VI summarizes the main conclusions to be drawn from this work.

II. EXPERIMENTAL

All species were studied as gases in the Berkeley Iron-Free Photoelectron Spectrometer.⁹⁾ Only ethylene (c.p. grade from Matheson Gas Co.) was purified somewhat by pumping at liquid nitrogen temperatures. The x-ray tube design is discussed elsewhere.¹⁰⁾ Oxide on the yttrium anode surface would be expected to produce $OK\alpha$ x-rays of energy near 525 eV. Thus photoelectrons ejected from the nitrogen 1s level of N_2 would be expected to fall under the outer three MO's obtained with $YM\zeta$ ¹¹⁾ (Fig. 1). Oxidation also manifests itself in broadened lines, due to the increase in x-ray linewidth. It therefore seems likely that oxide formation was not excessive in this case, since the MO's of nitrogen appear well-resolved. However, it should be noted that the outer three MO's shown in Fig. 1 were not scanned simultaneously with the $2\sigma_g$ peak, since oxidation increases with time. The area of $2\sigma_g$ relative to the remaining MO's was therefore not measured accurately.

Lorentzians were least-squares fitted to the experimental data points in each spectrum, with provision made for the satellites accompanying the main x-ray line.¹²⁾

III. NITROGEN AND CARBON MONOXIDE

The $YM\zeta$ spectra of nitrogen and carbon monoxide are shown in Figs. 1 and 2, respectively, together with the $MgK\alpha$ spectra from ref. 7.¹³⁾

The electronic structures of these isoelectronic molecules are very similar; this is reflected in both the MgK α and YM ζ results. In nitrogen, the orbital with the lowest intensity at 1253.6 eV photon energy, $1\pi_u$, becomes the strongest at 132.3 eV. The enhancement of orbitals with 2p character relative to those with 2s character at low photon energy has been observed previously in the fluoromethanes,¹⁾ as well as the hydride series.²⁾ Qualitatively, it can be understood by noting that the relative cross section for ionization from a certain orbital is larger the higher the overlap between this orbital and the outgoing electron wave. Thus, at the YM ζ energy, electrons emitted from molecular orbitals have a wavelength of $\sim 1.2 \text{ \AA}$, matching 2p orbitals better than 2s. The reverse is true at the MgK α energy where the $\sim 0.4 \text{ \AA}$ wavelength of a photoemitted electron matches the curvature of the inner lobe of the 2s function. From this simple argument, we conclude that $2\sigma_u$ must have considerable 2s character, since it is the most intense level at 1253.6 eV photon energy. *Ab initio* calculations¹⁴⁾ indeed support this, predicting a large 2s population in $2\sigma_u$. The monochromatized AlK α spectrum,⁵⁾ however, shows $2\sigma_g$ to be the most intense MO; $2\sigma_g$ also has substantial 2s character.¹⁴⁾ At 132.3 eV photon energy both $2\sigma_g$ and $2\sigma_u$ lose intensity relative to $2\sigma_u$ and $1\pi_u$. As mentioned earlier, $1\pi_u$ now possesses the highest intensity because it is of pure p parentage. The mixed s and p parentage of the $3\sigma_g$ orbital is confirmed by its behavior at low photon energy: it gains relative to the 2s-like $2\sigma_g$ and $2\sigma_u$, but loses relative to the 2p-like $1\pi_u$.

The intensity trends in CO are very similar to those in N₂, the most dramatic intensity change again occurring in the (purely 2p) 1π orbital.

In general, the outer three orbitals gain intensity relative to 3σ at the $Y\text{M}\zeta$ energy, due to their $2p$ character. The 4σ and 5σ orbitals also possess a large amount of oxygen $2s$ and carbon $2s$ character, respectively. The 4σ peak has the higher intensity at both 1253.6 eV and 132.3 eV.

Satellites were observed in both nitrogen and carbon monoxide. They are resolved most clearly in the monochromatized $\text{AlK}\alpha$ spectrum of Gelius *et al.*,⁵⁾ where the gases were studied at low pressure to eliminate energy-loss peaks. The $Y\text{M}\zeta$ spectra in Fig. 1 and 2 suggest that most of the satellite structure is associated with the outer three levels, because the intensity increases relative to the innermost MO. However, it is possible that some of the satellites may be configuration-interaction states of the deepest-lying MO. Shake-up structure associated with *core-level* ionization of nitrogen and carbon monoxide (Cl s) has been studied by Gelius.⁶⁾

Table I shows the experimental relative intensities at 1253.6 eV, 132.3 eV, 40.8 eV (He II), and 21.2 eV (He I) photon energies. The UPS (ultraviolet photoelectron spectroscopy) results were reported by Rabalais *et al.*,⁸⁾ who also integrated the areas under the $\text{MgK}\alpha$ spectra of Siegbahn *et al.*⁷⁾ to obtain the ratios listed in Table I. In the same table (columns 4 and 6), we also show theoretical cross section ratios from ref. 8,¹⁵⁾ at both the $\text{MgK}\alpha$ and $Y\text{M}\zeta$ energies. The calculations represent the ejected electron by a plane wave (PW), or a plane wave orthogonalized to the filled orbitals (OPW). Only PW results are listed in Table I, the OPW correction being small at the $Y\text{M}\zeta$ and $\text{MgK}\alpha$ energies. The frozen orbital approximation was assumed to hold for the filled orbitals, which were represented by linear combinations of Slater-type orbitals.

We note from Table I that the intensity ordering of the outer

three MO's in N_2 and CO is the same using He I, He II and YMc radiation. The same observation was made previously in the study of the second-row hydrides.²⁾ Theory predicts the correct intensity ordering of the outer three MO's in both N_2 and CO. The relative intensities of the $2\sigma_u$ and $2\sigma_g$ levels of N_2 and the 3σ level of CO at the YMc energy seem to be underestimated by the calculation. Part of the discrepancy may be due to the difficulty of curve-fitting the deepest lying MO in each of the two molecules. Furthermore, addition of the intensities of the shake-up peaks associated with the outer three levels should bring the intensity of the deepest lying MO more in line with theory. Of course, it is also possible that there may exist states associated with innermost MO ionization. However, the region on the high binding energy side of these MO's was not investigated. Fadley¹⁶⁾ showed that subshell cross section calculations based on the frozen orbital approximation actually yield the total cross section for single and multiple electron ionization associated with each subshell.

The relative intensities of the core levels are also listed in Table I. In determining the area ratios from the experimental spectra, Rabalais et al⁸⁾ stated that the change in spectrometer transmission with energy was not corrected for. Such a correction would improve the agreement of the N1s intensity with theory by raising its intensity to ~ 213 times that of $3\sigma_g$ instead of 145. (The correction is applied by multiplying by the kinetic energy ratios of the electrons in the respective peaks). The Cls to 5σ ratio obtained by Rabalais et al from Siegbahn's spectra appears to be too high, as does the relative area of O1s.

IV. ETHYLENE

Figure 3 shows the MgK α and YM ζ spectra of ethylene. With MgK α , it was not possible to distinguish the close-lying $1b_{2u}$, $3a_g$ and $1b_{1g}$ levels due to severe interference from the K α_{34} satellites of the more intense $2a_g$ and $2b_{3u}$ levels. The arrows in the figure point to their expected peak positions on the basis of UPS results.¹⁷⁾ Only one peak was employed in the least-squares fit to represent all three MO's. The monochromatized AlK α spectrum⁶⁾ shows the individual levels, but their areas appear somewhat uncertain due to the low intensity. Robin *et al.*¹⁷⁾ determined the orbital ordering from *ab initio* calculations. Their results were confirmed by Gelius,⁶⁾ using a simple model to predict relative intensities.¹⁸⁾

The MgK α spectrum was referenced to neon 2s (48.42 eV). However, only the binding energies of the three intense peaks in the spectrum could be determined accurately. The values are listed in Table II, together with the UPS results of the remaining MO's. With YM ζ , we were able to distinguish $1b_{1g}$, but $1b_{2u}$ and $3a_g$ again could not be meaningfully separated.

In both spectra a satellite was observed at ~ 27 eV, which had been obtained earlier with filtered AlK α radiation. It is clear from the MgK α spectrum that it must be largely if not entirely associated with $2a_g$ or $2b_{3u}$, judging from its high intensity. Gelius⁶⁾ also cited its high energy as an indication that it does not originate from any of the outer four MO's. The possibility of its being due to an energy loss is ruled out because two satellites of nearly equal intensity would be expected, corresponding to transitions in neutral ethylene induced by electrons from $2b_{3u}$ and $2a_g$.

A satellite was also observed in the core region (Fig. 4), which was scanned alternatively with the MO region in order to obtain relative intensities. The core satellite must be treated with care, since the possibility of energy loss cannot immediately be ruled out. It was studied with AlK α and at two different pressures. No change in relative intensity or position was detected. Our ethylene sample was c.p. grade, with a stated purity of at least 99.5%. A carbon containing impurity with such a high Cls binding energy (Cls of ethylene, 290.7 eV, plus 8.4 eV) almost certainly would contain fluorine. However, none could be detected when the Fls region was monitored. We therefore believe that the satellite corresponds to a state of ionized ethylene. The sloping background on the high binding energy side of Fig. 4 indicates that more structure may be present at higher binding energies. A preliminary run with AlK α showed this to be the case. However, the pressure dependence of those peaks was not examined.

It is interesting to note that the MO satellite is 8.13 eV away from $2b_{3u}$, which is close to the core satellite separation from the main peak (8.4 eV). Thus analogous transitions may be involved in both cases. It must be noted, however, that the core satellite is broader than the Cls peak (2.7(3) eV versus 0.84 eV). In contrast, the satellite in the MO region has a linewidth roughly comparable to that of $2a_g$ and $2b_{3u}$ (2.3(1) eV versus 2.02(4) eV for $2a_g$ and 1.81(4) eV for $2b_{3u}$). The broadening of the core satellite may indicate that more than one transition is involved. If a simple shake-up mechanism is invoked (monopole transition in the valence shell accompanying ionization), then two states would be expected, depending on the coupling of the three unpaired electrons in the

ion. Broadening may also be due to a short lifetime or to vibrational excitation.⁶⁾ The latter would be especially likely if the shake-up peak involves a transition from a bonding to an antibonding orbital, as is probably the case here.

The possibility that the core and MO satellites correspond to analogous transitions is further supported by the intensity analysis. We note that the core satellite is 21%, the intensity of Cls while the MO satellite is 42% the intensity of $2b_{3u}$ (39% the intensity of $2a_g$). Since the Cls peak is composed of two levels, $1a_g$ and $1b_{3u}$, of essentially the same binding energy, it seems possible that the shake-up transitions are associated with only one of them, most likely $1b_{3u}$ (judging from the energy separation discussed above).

Gelius⁶⁾ performed multiple-scattering-X α calculations¹⁹⁾ to determine the energy of the transition $1b_{1u} \rightarrow 1b_{2g}$ ($\pi \rightarrow \pi^*$) in the presence of a valence hole. Here $\pi \rightarrow \pi^*$ is a transition from the highest occupied orbital, $1b_{1u}$, to the lowest unoccupied orbital of ethylene, $1b_{2g}$. From optical data²⁰⁾ on the neutral species, the energies of the resulting $^3B_{3u}$ and $^1B_{3u}$ states are 4.6 eV and 7.6 eV, respectively. Gelius found an average energy of ~ 5.4 eV from the hole-state calculation. Accordingly, he proposed that a $2a_g$ vacancy is involved in the MO satellite, since the latter is 3.74 eV away from the $2a_g$ peak. The satellite was therefore assigned as the $^2B_{3u}$ state: $2a_g [1b_{1u} 1b_{2g}^* (^3B_{3u})]$ (underlining indicates removal of an electron), which interacts with the $^2B_{3u}$ state resulting from simple ionization of a $2b_{3u}$ electron. A similar assignment may be possible in the core spectrum provided the $1b_{1u} \rightarrow 1b_{2g}$ transition in the presence of a core hole is shown to have an energy close to 8.4 eV. If

the core hole is assumed localized, the symmetry of the ion is reduced to C_{2v} . The $\pi \rightarrow \pi^*$ transition thus becomes $b_2 \rightarrow b_2$, a monopole transition. Such an assignment seems possible, especially since the energy of the satellite is in good agreement with the $lb_{1u} \rightarrow lb_{2g}$ transition to ${}^1B_{3u}$ in the neutral species. However, more detailed calculations are needed to determine whether a configuration interaction state or a simple shake-up state is involved in the observed satellites.

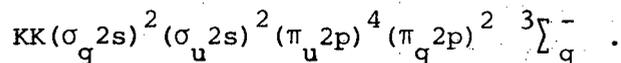
The change in the relative intensities of the various orbitals with photon energy is qualitatively the same as in N_2 and CO. At 1253.6 eV, the outer four orbitals have low intensity because they are predominantly 2p in character. When the exciting radiation energy is lowered to 132.3 eV, they gain intensity relative to $2a_g$ and $2b_{3u}$. With regard to relative intensities, the spectrum of ethylene is reminiscent of that of methane,¹⁾ both at the $YM\zeta$ and the $MgK\alpha$ energy.

In Table II we list the experimental intensity ratios obtained with 21.2 eV,⁸⁾ 40.8 eV,⁸⁾ 132.3 eV and 1253.6 eV photons. The relative intensities do not seem to change by much in going from He I to He II radiation in this case. Both resemble the intensity ratios with $YM\zeta$ radiation, except for the $2b_{3u}$ and $2a_g$ relative intensities. The theoretical results of Rabalais et al.⁸⁾ at 1253.6 eV and 132.3 eV are shown in columns 3 and 5 respectively. Only the intensity ordering of $3a_g + lb_{2u}$ relative to lb_{1u} (at 132 eV) is reversed by the calculations. Addition of the satellite intensity to $2b_{3u}$ brings it into very good agreement with theory at 132 eV. This is not the case at 1254 eV, however. The theoretical Cls relative intensity is too low, even without adding the area of the satellite to the experimental area of the main peak.

V. OXYGEN

The spectra taken with MgK α and YM ζ x-rays are shown in Fig. 5. Only the region below ~ 30 eV binding energy was studied. Essentially the same region (12 - 28 eV) has been studied previously with the 21.2 eV and 40.8 eV He lines.²¹⁾ The entire MO spectrum with MgK α was reported earlier by Siegbahn et al.,⁷⁾ referenced to the Ar 2p_{3/2} line.

The ground state electronic configuration of molecular oxygen is:



Ionization from the $\pi_g 2p$ yields one doublet state, $X^2\Pi_g$. This level appears well-resolved in our spectra, and therefore constitutes a good energy reference for the remaining states. Its vertical ionization potential of 12.33 eV (from UPS²¹⁾) disagrees with the value of Siegbahn et al.⁷⁾ (13.1 eV). Other spectroscopic techniques²²⁾ also yield an $X^2\Pi_g$ energy of 12.3 eV. Edqvist et al.²¹⁾ measured a ${}^2\Pi_{1/2} - {}^2\Pi_{3/2}$ spin-orbit splitting of 23 meV. Such a small splitting is of course beyond the resolution capabilities of XPS. The intensity of the $X^2\Pi_g$ state relative to the $\sigma_u 2s$ levels is much enhanced in going from the MgK α to the YM ζ spectrum, which is not surprising since this state is entirely 2p in character by symmetry.

Ionization from the fully occupied $\pi_u 2p$ orbital may yield the following states: $a^4\Pi_u$, $A^2\Pi_u$, ${}^2\Pi_u$, ${}^2\Pi_u$ and ${}^2\Phi_u$. As Edqvist et al.²¹⁾ point out, ${}^2\Phi_u$ cannot be reached by a one-electron transition from the ground state of O₂ and would therefore not be expected to appear in the photoelectron spectrum. The $a^4\Pi_u$ and $A^2\Pi_u$ states are severely overlapped

in the UPS spectrum, and can only be separated by careful deconvolution of the two vibrational progressions.²¹⁾ Since their vertical I.P.'s differ by 1 eV (see Table III), it might have been possible to deconvolute them in the XPS spectrum had it not been for the interference of the $b^4\Sigma_g^-$ state at 18.2 eV. As it is, only the $a^4\Pi_u$ state could be distinguished clearly, and its energy is in excellent agreement with the UPS result.

It is interesting that the intensity ordering of the partially resolved peaks at 16.7 eV and 18.2 eV is reversed in going from the MgK α to the YMc spectrum, confirming the 2s character of $b^4\Sigma_g^-$ and the 2p character of $a^4\Pi_u$.

In least-squares fitting our experimental spectra we found that the two innermost peaks of the MgK α spectrum are best represented by Gaussians. The remaining peaks may be fitted well with either Gaussians or Lorentzians. We only show the Gaussian fit in Fig. 5, but in Table III we list area ratios from both.

With the aid of the quantitative relative intensities obtained by curve fittings, it is possible to confirm the existence of $A^2\Pi_u$ which is otherwise very difficult to observe directly by XPS due to insufficient resolution. Since this state is separated from $b^4\Sigma_g^-$ by only ~ 0.5 eV (see Table III), the peak at ~ 18 eV must be a composite of the two states. Now the ratio of $b^4\Sigma_g^-$ to $B^2\Sigma_g^-$ would not be expected to change by much when the excitation energy is changed. From Table III, the relative intensity of the ~ 18 eV peak ($b^4\Sigma_g^- + A^2\Pi_u$) to the $B^2\Sigma_g^-$ peak increases by a factor of ~ 2 when the MgK α is replaced with YMc (taking the average of the Gaussian and Lorentzian fits), indicating the presence

of a 2p-like state which gains in intensity at the YMζ energy.

Dixon and Hull²³⁾ performed semi-empirical configuration interaction calculations on the oxygen ion resulting from Π_u ionization to determine the relative intensities of the different Π_u states. They predicted an intensity ratio of a $4\Pi_u$ to the three $2\Pi_u$ states of 2:0.34:0.001:0.64. Edqvist et al²¹⁾ found an experimental $4\Pi_u$ to $A^2\Pi_u$ ratio of 2:0.3. They also identified the diffuse band at 24.0 eV in the He II spectrum as $2\Pi_u$, since its intensity relative to a $4\Pi_u$ is 0.75:2. Our YMζ spectrum shows definite evidence for a state at 23.5 eV. The same state in the MgKα spectrum can be obtained by a deconvolution. It is clear from Fig. 5 that the resolution with MgKα is comparable to that with YMζ in this case. Thus the state at 23.5 eV must have a higher intensity at 132 eV relative to $c^4\Sigma_u^-$ than at 1254 eV. This confirms its p character and its assignment as $2\Pi_u$. Our energy value is somewhat lower than the UPS result, however.

The energies of the $c^4\Sigma_u^-$ and $2\Sigma_u^-$ states are ~ 0.8 eV lower than the values reported by Siegbahn et al⁷⁾ (25.3 eV and 27.9 eV respectively). Furthermore, the energy of $c^4\Sigma_u^-$ differs by almost 3 eV from the UPS results. Our measured splitting of 2.74(3) eV (MgKα value), on the other hand, agrees better with the 2.6 eV result of ref. 7. It is interesting that the multiplet splitting in the MO region is a factor of two larger than the core splitting (1.1 eV). This is due to the larger exchange integrals between the unpaired electron of the ionized level and the electrons in the π_g orbital.²⁴⁾

The area ratio of $c^4\Sigma_u^-$ to $2\Sigma_u^-$ appears to be in excess of the degeneracy value of 2. Positive deviations from the multiplet ratio have been observed in the core spectrum of a number of systems.²⁵⁾ In

the present case part of the deviation may be an artifact of the fitting procedure. Dixon and Hull²³⁾ found a $a^4\Pi_u/{}^2\Pi_u$ ratio of 2:0.64, which appears to disagree with our experimental relative intensity of 2:1.3(6) with MgK α and 2:0.26(7) with YM ζ . However, the experimental results must be interpreted cautiously since the area of a ${}^4\Pi_u$ may contain contributions from the unresolved $A^2\Pi_u$ state. The latter is separated from a ${}^4\Pi_u$ by 1 eV (see Table III) and is predicted to have an intensity 0.17 that of a ${}^4\Pi_u$. In view of this, the agreement with the calculation of Dixon and Hull must be considered satisfactory.

VI. CONCLUSIONS

The YM ζ spectra reported in this work further establishes the value of this 132.3 eV photon source as a useful tool in molecular photoelectron spectroscopy. A number of orbital assignments in N_2^+ , CO^+ , $C_2H_4^+$, and O_2^+ were established or confirmed by comparison of soft (1253.6 eV) and ultra-soft (132.3 eV) x-ray photoemission spectra:

1. The atomic-orbital compositions of the N_2 and CO molecular orbitals in N_2 and CO were unequivocally confirmed, and the similarity of these molecules was displayed in detail, by comparison of relative intensities from 1253.6 eV to 132.3 eV.
2. The outer four orbitals in C_2H_4 are emphasized in the YM ζ spectrum, and their p character is established.
3. In O_2 , the outer orbitals are also more clearly emphasized. The $A^2\Pi_u$ is shown to be present, and the ${}^2\Pi_u$ state at 23.5 eV is seen directly. Improved binding energies were obtained.

These spectra provide a definitive test of the cross section ratios at these energies calculated with plane-wave or OPW final states. Qualitative trends are predicted in most cases, and the theory at this level has some diagnostic value. Quantitative argument is lacking however. Thus, for example, we could use these calculations together with our spectra to decide the ordering of orbitals, but not to decide between two sets of similar wave functions describing them.

Finally the advantages of the YMc line for studying adsorbed molecules are rather obvious. Photoemission at this energy has much greater surface sensitivity than at 1253.6 eV, and is not plagued by the final-state distortion encountered at UPS energies. The use of YMc and $MgK\alpha_{12}$ lines with the same sample should be an especially powerful diagnostic device, because different orbitals are emphasized at the two energies.

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TABLE II. Ethylene binding energies and differential photoionization cross section ratios.

Orbital	E_B (eV)	$I_{\text{exp}}(\text{MgK}\alpha)$	$I_{\text{theo}}(\text{MgK}\alpha)^{\text{a)}$	$I_{\text{exp}}(\text{YM}\zeta)$	$I_{\text{theo}}(\text{YM}\zeta)^{\text{a)}$	$I_{\text{exp}}(\text{He II})^{\text{a)}$	$I_{\text{exp}}(\text{He I})^{\text{a)}$
$1b_{1u}$	10.51(4) ^{c)}	0.05(2)	0.015	0.9(2)	4.42	0.9	0.9
$1b_{1g}$	12.85 ^{c)}		0.017	0.6(4)	2.20	1.12	1.31
$3a_g$	14.66 ^{c)}	0.35(9)	0.023		1.96	1.33	1.41
		$(1b_{1g} + 3a_g + 1b_{2u})$		2.4(2)			
$1b_{2u}$	15.87 ^{c)}		0.033	$(3a_g + 1b_{2u})$	1.84	1.02	0.89
$2b_{3u}$	19.23(2)	0.93(3)	0.68	1.2(1)	1.34	0.21	0.20
$2a_g^{\text{b)}$	23.65(2)	1.00	1.00	1.00	1.00	0.24	--
MO shake-up	27.39(5)	0.39(6)	--	0.2(4)	--	--	--
$1a_g, 1b_{3u}$	290.7 ^{d)}	69.98(3)	43.6	--	--	--	--
core shake-up	299.10(7)	14.87(9)	--	--	--	--	--

a) Reference 8, theoretical values communicated to us by J. W. Rabalais.

b) Theoretical σ_1 is $5.83 \times 10^{-21} \text{ cm}^2$ at 132 eV and $2.00 \times 10^{-22} \text{ cm}^2$ at 1254 eV.

c) UPS results of ref. 17.

d) T. D. Thomas, J. Chem. Phys. 52, 1373 (1970).

TABLE III.

State	E_B (MgK α)	E_B (YM ζ)	E_B (He) ^{a)}	Area (MgK α) ₁ ^{b)} Ratio	Area (MgK α) ₂ ^{c)} Ratio	Area (YM ζ) Ratio
$x^2\Pi_g$	12.33(2) ^{d)}	12.33(1) ^{d)}	12.33	1.00(3)	1.00(7)	1.00(2)
$a^4\Pi_u$	16.70(2)	16.72(2)	16.70	1.41(4)	1.0(1)	1.00(5)
$A^2\Pi_u$	--	--	17.73	1.51(4)	1.7(1)	0.71(7)
$b^4\Sigma_g^-$	18.17(2)	18.09(2)	18.17			
$B^2\Sigma_g^-$	20.39(7)	20.42(3)	20.43	1.0(1)	0.7(1)	0.22(9)
$^2\Pi_u$	23.0(4)	23.47(6)	24.0	0.9(6)	--	0.13(5)
$c^4\Sigma_u^-$	24.51(2)	24.56(2)	27.4	6.58(7)	--	0.65(4)
$^2\Sigma_u^-$	27.25(2)	26.96(8)	--	2.31(4)	--	0.2(2)

a) From ref. 21.

b) Gaussian fit.

c) Lorentzian fit.

d) Reference value.

FIGURE CAPTIONS

- Fig. 1. Nitrogen photoemission spectra taken with MgK α x-rays (top) and YM ζ x-rays (bottom). MgK α spectrum is reproduced from ref. 7. The outer three MO's in the YM ζ spectrum were not scanned simultaneously with $2\sigma_g$ and the area ratio is therefore approximate.
- Fig. 2. Carbon monoxide photoemission spectra taken with MgK α x-rays (top) and YM ζ x-rays (bottom). The MgK α spectrum is taken from ref. 7.
- Fig. 3. Ethylene spectra taken with MgK α x-rays (top) and YM ζ x-rays (bottom). Counts were obtained at increments of ~ 0.3 eV with MgK α and ~ 0.2 eV with YM ζ .
- Fig. 4. Core spectrum of ethylene taken with MgK α x-rays. Counts were obtained at increments of ~ 0.3 eV.
- Fig. 5. Oxygen spectrum in the region up to 32 eV binding energy. Counts were obtained at increments of ~ 0.16 eV in the MgK α spectrum (top) and ~ 0.2 eV in the YM ζ spectrum (bottom).

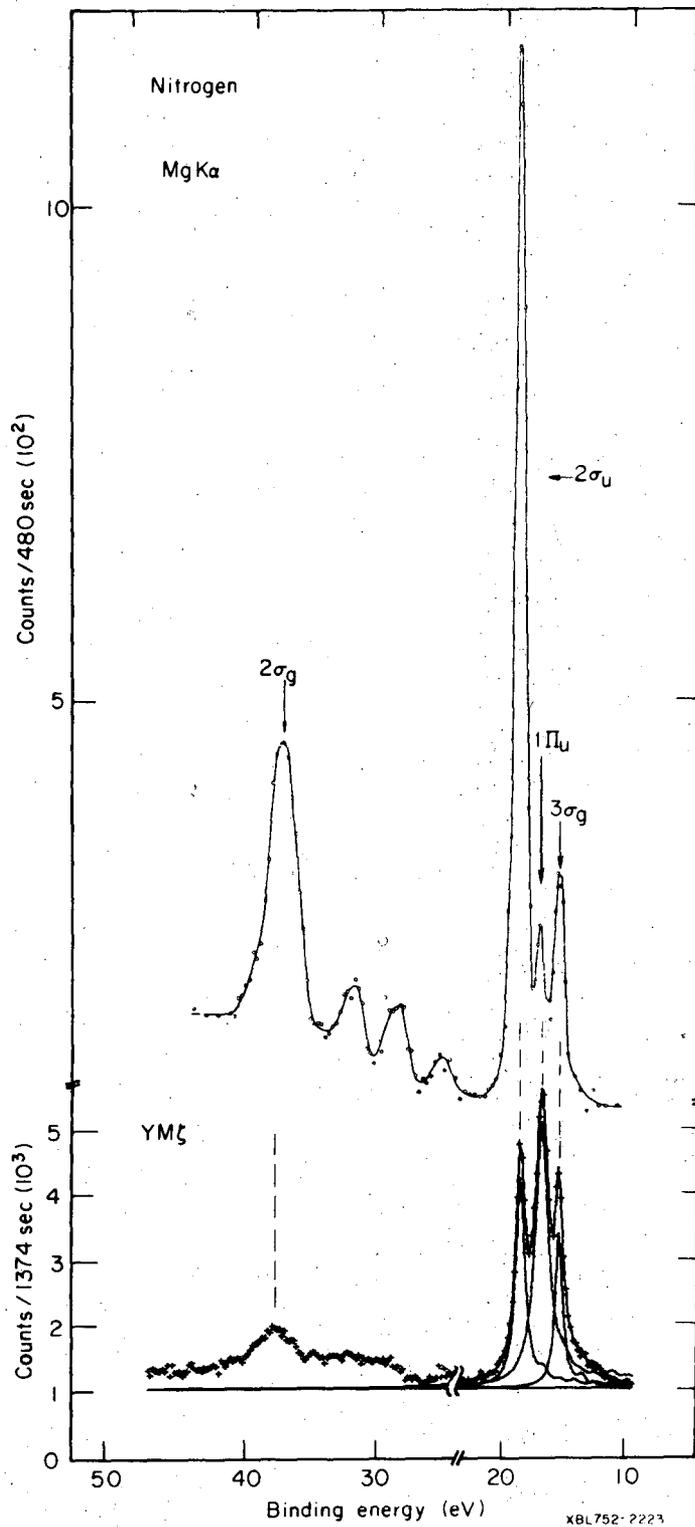
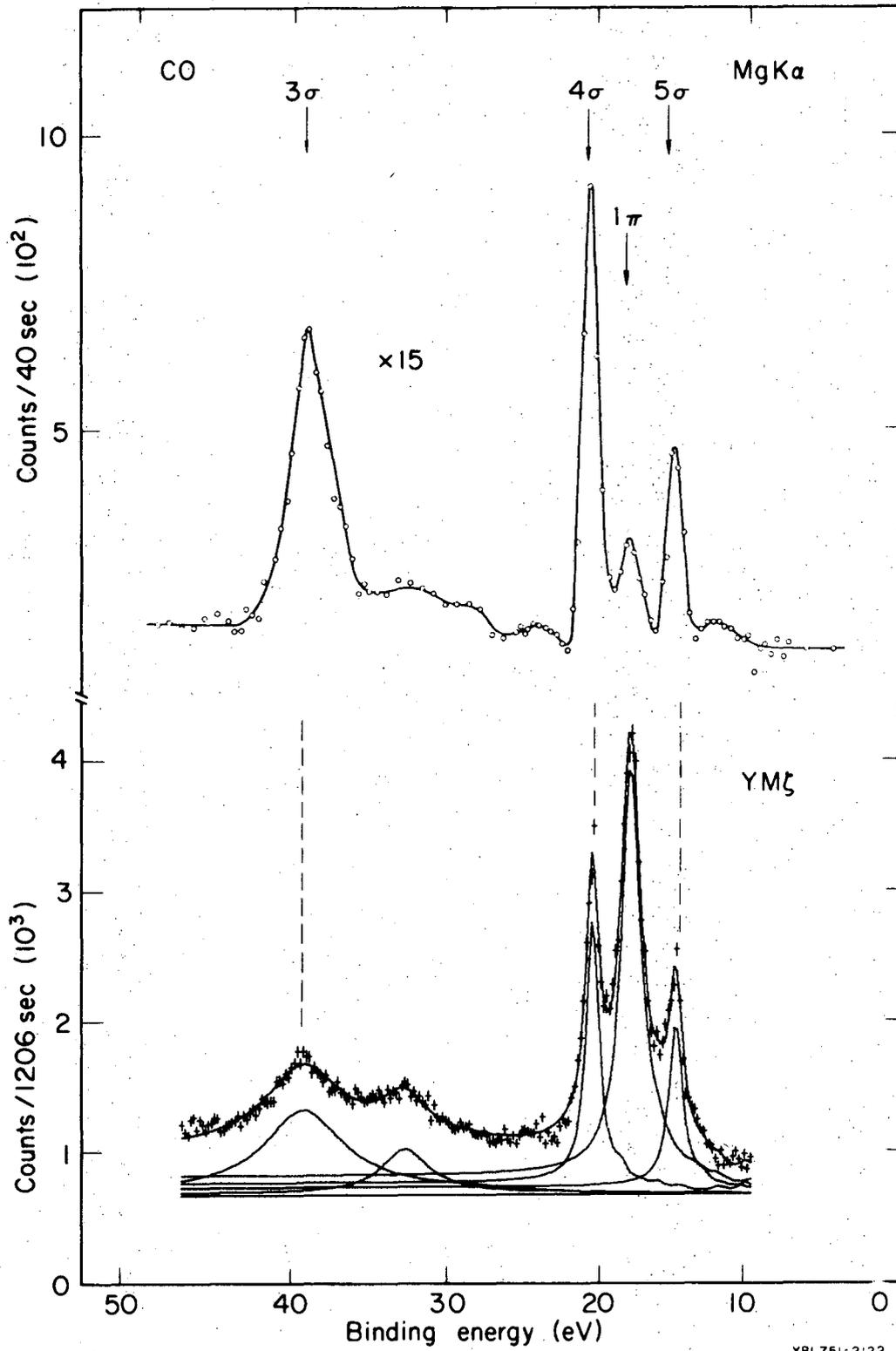
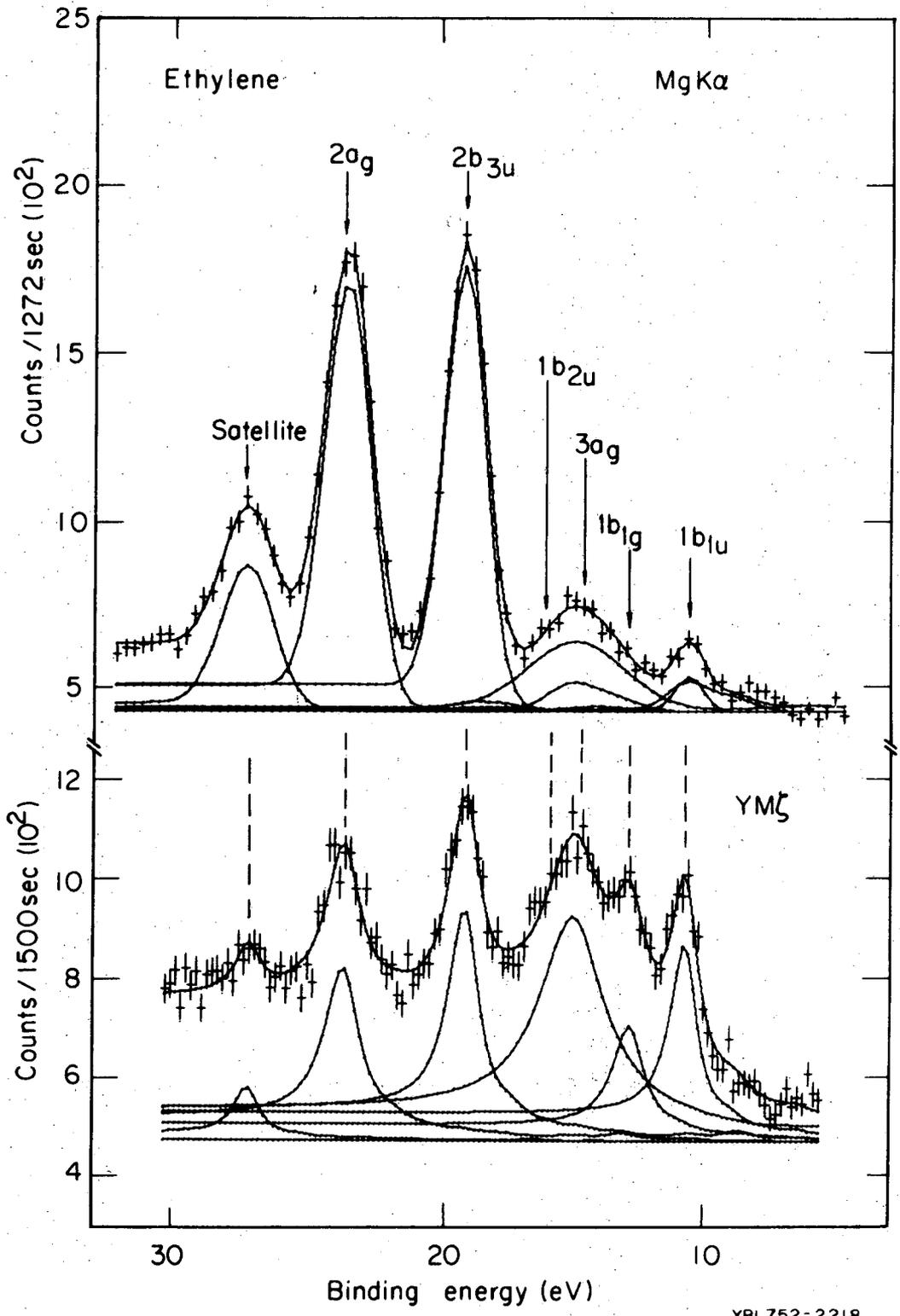


Fig. 1



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Fig. 2



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Fig. 3

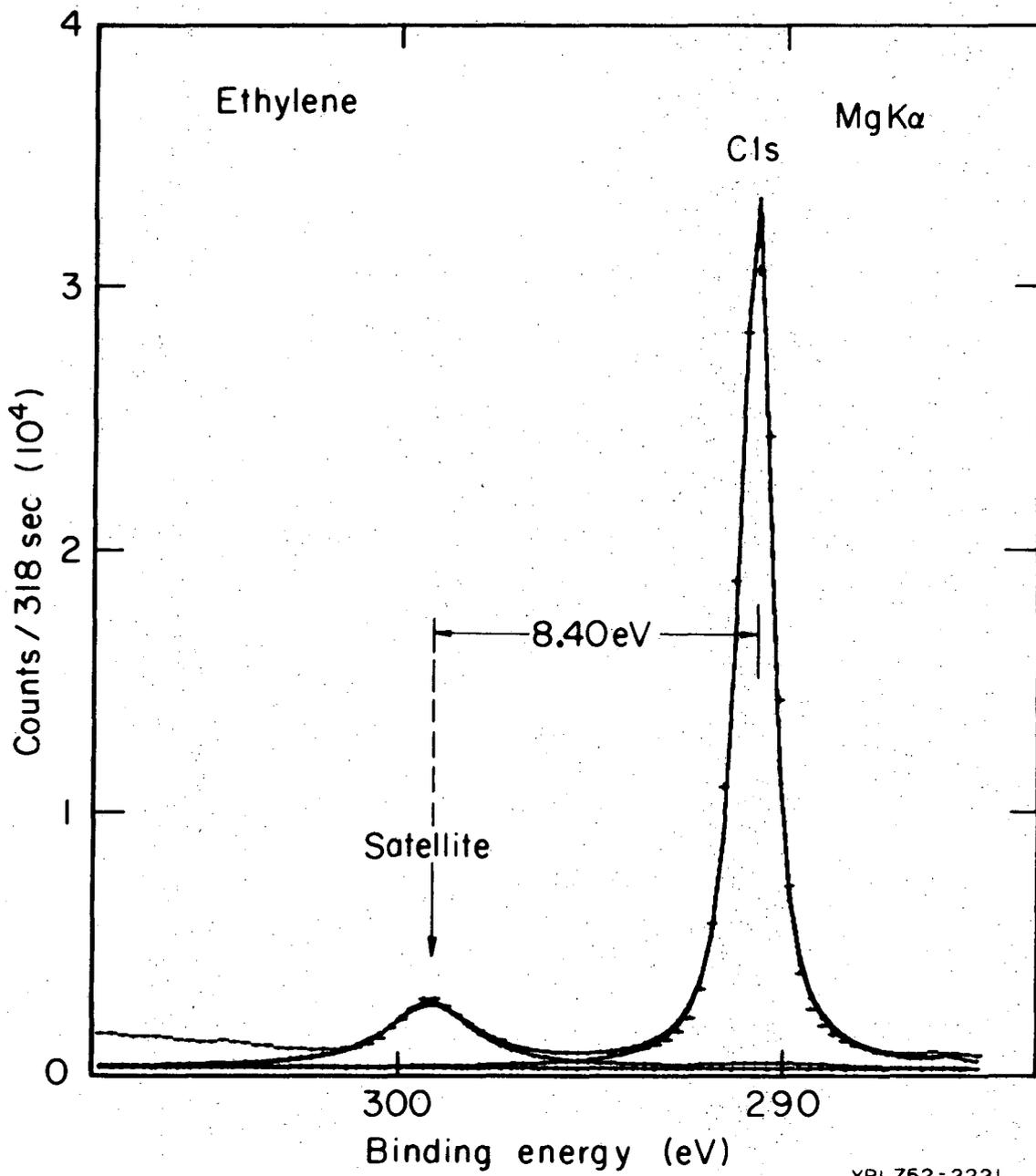
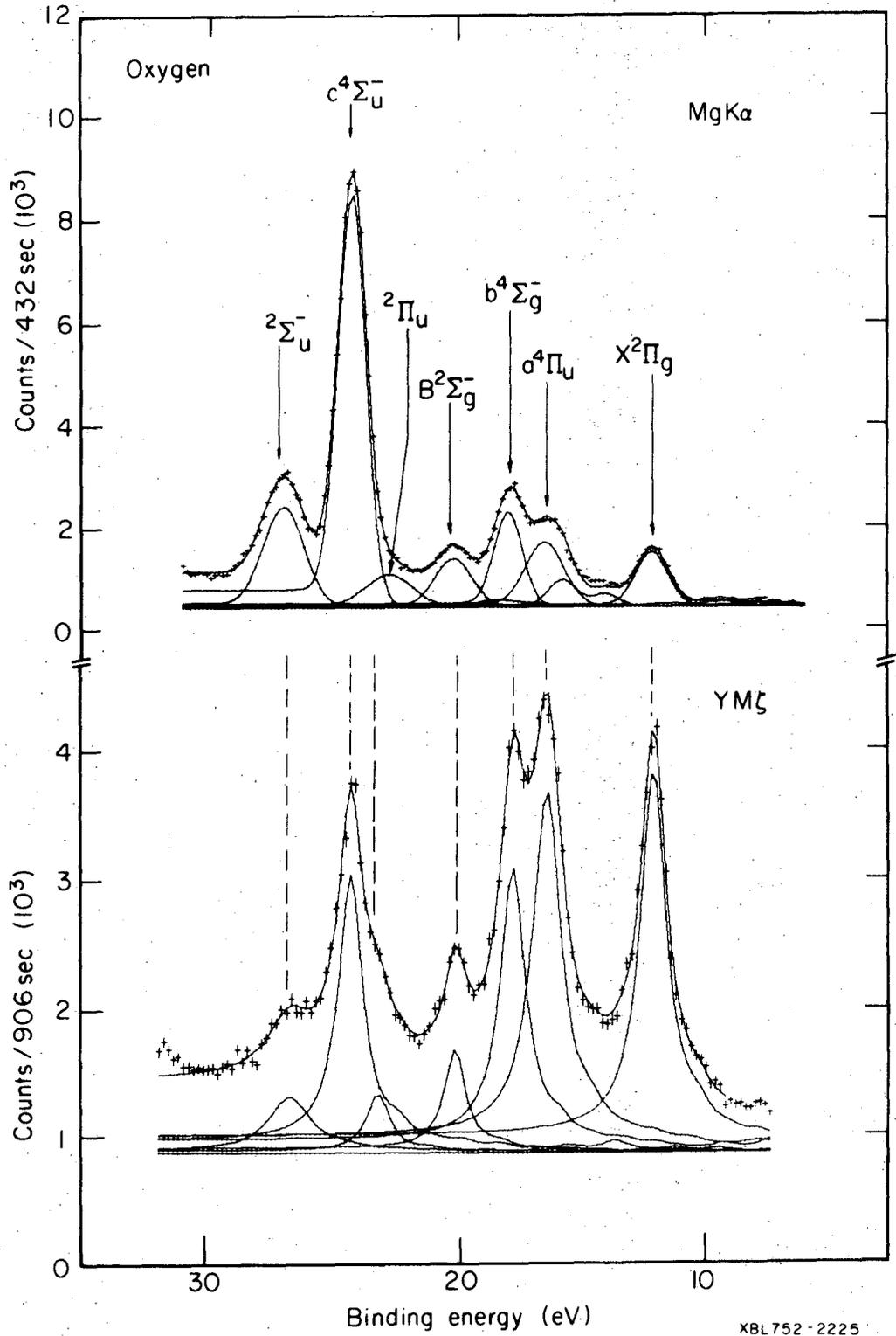
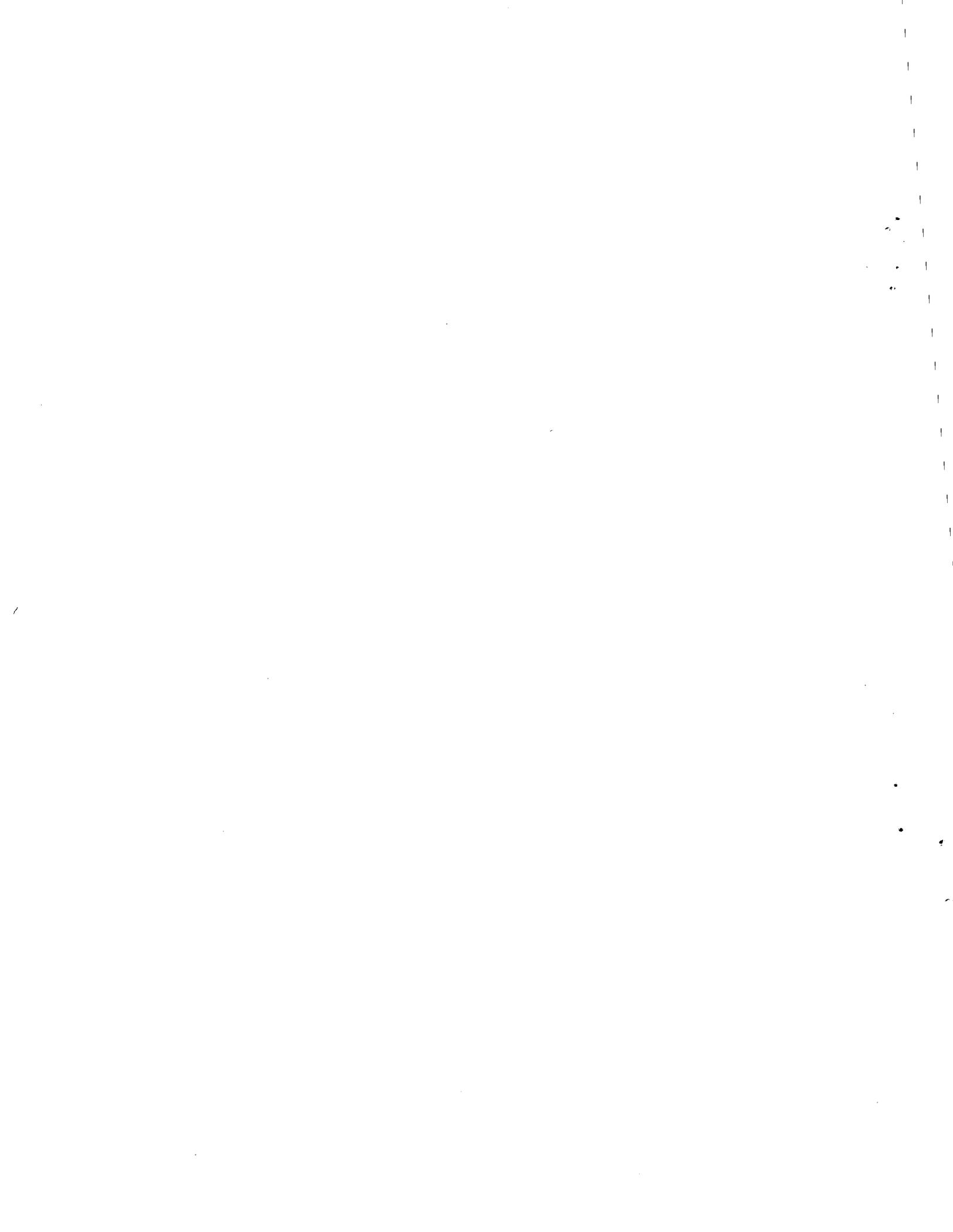


Fig. 4



XBL752-2225

Fig. 5



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