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M. S. Banna and D. A. Shirley

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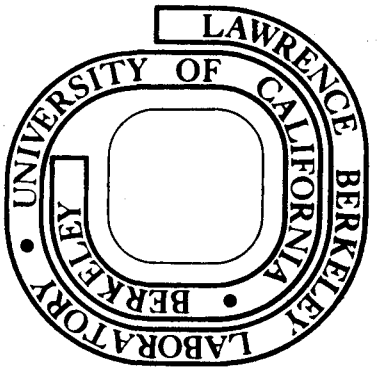

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LBL-3491

ON THE USE OF YTTRIUM AND SODIUM ANODES IN PHOTOELECTRON SPECTROSCOPY *

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ABSTRACT: Low-cost anodes of the active metals yttrium and sodium were constructed and used under modest vacuum conditions. The yttrium $M\zeta$ line (132.3 eV) was used to determine np/ns cross section ratios in the valence shells of three rare gases. The $NaK\alpha_{12}$ line and its satellites were characterized with a neon converter. It yielded a line-width of 0.58(1) eV on the neon 1s line, from which an upper limit of 0.42 eV was set for the $NaK\alpha_{12}$ x-ray linewidth. On several "test cases" the $NaK\alpha_{12}$ x-ray fell between other characteristic x-rays (e.g., $MgK\alpha_{12}$) and monochromatized sources in its ability to resolve fine structure. The methane C1s peak was asymmetric and the correct vibrational spacing was obtained by fitting with three components of the correct intensity ratios. Similarly, relative chemical shifts of the unsubstituted carbons in m-difluorobenzene were determined almost completely by fitting the asymmetric peak. In the PF_5 (F1s) and O_2 (O1s) cases some new information was obtained.

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I. INTRODUCTION

As photoelectron spectroscopists turn their attention increasingly toward synchrotron radiation sources to obtain variable energy and highly monochromatic radiation, it is important not to neglect the development of conventional x-ray line sources. This paper reports exploratory applications of two narrow-line sources -- yttrium Mζ (132.3 eV)[1] and sodium Kα (1041.0 eV)[2] to x-ray photoemission spectroscopy (XPS). These sources were developed at relatively low cost for use in the Berkeley Iron-Free Photoelectron Spectrometer. It should be possible to incorporate them into any XPS machine operating under moderate vacuum conditions (10^{-6} to 10^{-7} torr).

The importance of varying the photon energy in XPS studies has been underscored in recent years. For example, Wuilleumier and Krause[3] utilized sixteen different anode materials to study photoionization in neon gas. This made possible a complete partitioning of the photoelectric cross section among the different ionization events. A rigorous test of theoretical cross section calculations could be applied. Banna and Shirley[4-6] reported gas-phase spectra of several molecules, using the YMζ line introduced into photoelectron spectroscopy by M. O. Krause,[1] in conjunction with the conventional $MgK\alpha_{12}$ (1253.6 eV) x-ray. These studies indicated that the cross-section variation with x-ray energy could be used to advantage in making orbital assignments.

In 1967 Siegbahn et al.[7] produced sodium Kα x-rays from a sodium-gold alloy and used them to obtain a 1.3 eV FWHM carbon 1s photoelectron peak from graphite. We are aware of no further published work with the NaKα line, but R. G. Cavell first showed the feasibility of the experi-

mental approach used in this paper.[8] This line combines the advantage of good resolution with a photon energy sufficiently high to photoionize electrons from the 1s shells of second-row elements. In this work we have been particularly interested in determining the line widths and intensities obtainable in NaKα XPS spectra under modest vacuum conditions.

In Section II we describe how the yttrium and sodium anodes were prepared. Section III reports valence s/p cross section ratios obtained with the YMζ line. In Section IV the NaKα main line and neighboring satellites are reported, using a neon converter. Spectra are reported of several molecules that were carefully selected to test the ability of the NaKα line to resolve close-lying peaks in cases of chemical interest. Conclusions are given in Section V.

II. EXPERIMENTAL

The Berkeley Iron-Free Photoelectron Spectrometer was equipped with two new x-ray tubes for the production of YMζ and NaKα x-rays, respectively. In Fig. 1, we show the major components of the yttrium x-ray tube. Because of its proximity to the ionization chamber, the filament was wound noninductively, as shown. The filament support rods could then be mounted no more than 3 mm apart, thus minimizing the net field. An insulated 'hook' was used to support the right end of the filament.

An yttrium disk was cut from rod stock and press-fitted into a copper cup with a slightly smaller inside diameter. Cooling water was delivered to the copper backing. A positive potential was applied to the anode, while the filament was maintained at ground potential. In

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order to focus the electron beam, a grounded stainless steel shield concentric with the anode was used. The x-ray tube walls were also grounded and were cooled to prevent overheating of the window.

Formvar films $\sim$ 20 $\mu gm/cm^2$-thick were chosen to transmit YMζ x-rays because they formed an adequate vacuum seal when spread over a smooth copper surface with a 9.5 mm diameter window opening. No leakage through the films could be detected during operation, with a gas pressure of 10^{-1} torr in the target chamber and 10^{-7} torr in the x-ray tube. Window lifetimes of 24 hours or longer were possible as long as direct irradiation by the filament was avoided.

Krause has shown[16] that photoelectron lines as narrow as 0.6 eV (Ne 2p) are attainable with YMζ x-rays. However, oxide formation on the anode surface can lead to considerable broadening. For this reason it was necessary to operate our x-ray tube at +5.5 kV anode voltage, in order to sample more of the bulk yttrium. Still, the ultimate linewidth was rarely achieved.

In contrast to the yttrium x-ray tube design, the filament was raised to a high *negative* potential in the sodium source arrangement, with the x-ray tube walls and anode at ground potential. This was possible in this case because 0.005"-thick beryllium windows could be used, which are considerably more resistant to electron bombardment than formvar films. Sodium was cut under heptane and loaded into two holes made in the cathode block surrounding the filament.[8] When the filament was heated the sodium evaporated onto the anode surface. Copper or gold-plated copper anodes were used. A 7 - 8 kV potential was applied to the filament, with an emission current of 20 mA. We did not increase the power much further

to avoid evaporating the sodium off the anode surface. The resulting photoelectron intensities were $\sim$ 1/4 of those obtainable with $MgK\alpha_{12}$ produced at 14 kV and 20 mA. An initial decrease in intensity was observed, followed by a slower decrease over a period of more than 24 hours.

We emphasize that the present NaKα anode design is preliminary. One highly desirable modification would be to employ a separate heater for the sodium, to allow repeated deposition. A fresh sodium layer is important to increase the intensity and prevent line broadening due to x-rays from oxidized sodium.

Electrons emitted perpendicular to the direction of the unpolarized x-ray beam ($\theta = 90°$) were focused with a resolution of $\frac{\Delta E}{E} = 6 \times 10^{-4}$ and detected by a Bendix Channeltron electron multiplier. Experimental peaks were least-squares-fitted with Lorentzian functions (Gaussian in the case of the fluorine 1s level of PF_5), enabling the determination of positions, areas and linewidths.

III. RARE GAS VALENCE SUBSHELL INTENSITY RATIOS

The study of the rare gas series offers an opportunity to examine relative cross section changes with principal quantum number. In Table I we list the valence p/s ratio for neon, argon and krypton with 1253.6 and 132.3 eV radiation. The argon spectra are shown in Fig. 2. We were unable to obtain the valence spectrum of xenon with 132.3 eV photons, probably due to the low photoelectric cross section, coupled with low x-ray intensity.

The np/ns intensity ratios obtained with the YMζ x-ray had high statistical accuracies, but they were subject to systematic errors that were difficult to estimate. These errors are particularly troublesome

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for low energy electrons, as they arise from various scattering processes as well as possible variations in detector efficiency. Conservative error estimates are given in Table I to take possible systematic errors into account.

The ratios of Spears, Fischbeck and Carlson[9] at 1253.6 eV, as well as those of Siegbahn et al.[10] agree quite well with ours except for Kr, in which case our value lies between the other two. Spears et al. also reported the 3p/3s ratio of argon with ZrMζ x-rays (151.4 eV),[1] which would not be expected to be much different from the ratio at 132.3 eV photon energy. As seen in Table I, the agreement is excellent.

Both the MgKα and YMζ ratios show a definite trend. At 132.3 eV, the valence p/s ratio decreases in going from neon to krypton, while the opposite is true at 1253.6 eV. Simple overlap arguments, inspired by the work of Cooper[11] and Price et al.[12] can be invoked to explain this trend qualitatively. For a fixed x-ray energy, let us assume a plane wave for the outgoing electron with a wavelength roughly the same for ionization from s or p ($\sim$ 1.2Å with YMζ and $\sim$ 0.35Å with MgKα). At 132.3 eV, this wavelength is such that the outgoing electron overlaps better with the diffuse and nodeless 2p orbital of neon than with the contracted 2s orbital, the overlap being proportional to the photoelectric cross section. As one proceeds to argon, then krypton, the outer p orbital acquires first one then two nodes, making for less overlap with the outgoing electron wave. The s orbital, on the other hand, becomes more diffuse as the total number of shells is increased. A more diffuse s wavefunction overlaps better with the photoejected electron wave.

With 1253.6 eV photons, the outgoing electron wavelength is about

0.35Å. Better overlap would therefore be expected with neon 2s rather than neon 2p, the overlap with s orbitals decreasing in argon and krypton relative to the overlap with p orbitals. The s orbitals match the photoelectron wavelength less as they become more diffuse; the p orbitals match it more as they acquire nodes.

IV. THE NaKα PHOTOEMISSION SPECTRA

The satellites accompanying the main $K\alpha_{12}$ line in the sodium x-ray spectrum were studied using the neon 1s level as a converter. The spectrum is shown in Fig. 3. A least-squares fit yielded the following satellites (positions, intensities) relative to the main $K\alpha_{12}$ peak: Kα' (4.00 eV, 0.02), $K\alpha_3$ (7.00 eV, 0.12), $K\alpha_4$ (8.52 eV, 0.094).[13] In order to reproduce the slight asymmetry on the high binding energy side of the main peak, subsequent least squares fits were made using two peaks to represent the x-ray form, with a separation of 0.18 eV and an area ratio of 2.2:1.[14] (The smaller peak has the higher binding energy.)

Figure 4 shows the narrowest Ne 1s peak we were able to obtain: 0.58(1) eV FWHM. Using the same spectrometer resolution of $\Delta E/E = 6 \times 10^{-4}$, the corresponding Ne 1s linewidth with MgKα photons is 0.69(1) eV. From the width of the Ne 1s ($NaK\alpha_{12}$) photoelectron peak it is possible to estimate an upper limit for the $NaK\alpha_{12}$ x-ray linewidth. The Ne 1s level is known to be close to 0.23 eV[15] wide. If we assume that the Ne 1s level width and the $NaK\alpha_{12}$ x-ray width add quadratically and the spectrometer contribution adds linearly, we obtain $\Delta E = 0.42$ eV for the FWHM of the $NaK\alpha_{12}$ line. Although this is an upper limit, it is probably fairly close to the true value. From the 0.23 eV 1s linewidth and the known[16]

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spin-orbit splitting in neon we estimate the effective $NeK\alpha_{12}$ linewidth as 0.29 eV FWHM, and the $NaK\alpha_{12}$ value should be a little larger.

We turn now to several test cases for the $NaK\alpha_{12}$ line. Figure 5 shows the carbon 1s spectrum of methane, previously studied in detail with monochromatized $AlK\alpha$ x-rays by Gelius et al,[15] who were able to obtain both the ratios and energy separations of the three vibrational levels under the main peak. Using their intensity ratios in our fitting procedures, we obtained separations of 0.43(2) eV and 0.41(7) eV between the vibrational levels in order of increasing binding energy, in excellent agreement with the monochromatized x-ray value of 0.43(2) eV obtained by Gelius et al. Lorentzians constrained to have equal linewidth were used to fit the composite peak. While the monochromatic source of Gelius et al. gives appreciably better resolution of the vibrational components in CH_4, the spectrum shown in Fig. 5 is distinctly superior to results obtained heretofore with other characteristic x-rays. We note that the asymmetry in the composite peak is obvious by visual inspection, and the ability of these data to yield the correct separations in the least-squares fit reinforces this observation. We believe that with a better spectrometer it would be possible to achieve considerably better resolution of the three C1s components in the $CH_4(NaK\alpha_{12})$ spectrum.

Next we consider a case of more direct chemical interest: the C1s photoelectron spectrum in m-difluorobenzene. The fluorinated benzenes were studied by Davis et al.[17] in the gas phase and by Clark et al.[18] as solids. Davis et al. did not attempt to resolve components of the C1s peak arising from unsubstituted carbons. Clark et al. drew tentative conclusions about these components, but their conclusions had no direct

experimental basis, as they used a combination of DuPont "curve resolver" and theory. Figure 6 shows the Cls photoelectron spectrum of m-difluorobenzene obtained with $NaK\alpha_{12}$ radiation. The peak at 293 eV clearly belongs to the fluorine-substituted carbons (carbons 1 and 3). The more intense peak at 291 eV, belonging to the four unsubstituted carbons, is clearly made up of at least two components. It is wider, less than twice as high, asymmetric, and flat-topped. In this molecule, vibrational fine structure should be too closely-spaced to create such an asymmetry, and it can be attributed to core-level binding energy shifts. Carbons 4 and 6 must have the same binding energies by symmetry, while carbons 2 and 5 can have unique energies. There are thus three components of relative intensities 1:1:2. Since the 291 eV peak is asymmetric on the high-binding energy side, the high intensity component from carbons 4 and 6 must lie on the low-binding energy side of this peak. Up to this point our conclusions are based on visual inspection and logic. The assignment of carbons 4 and 6 to the low-binding energy side of the 291 eV peak agrees with the theoretical prediction[19] of Davis et al[17] and with the conclusions of Clark et al.[18] The two peaks corresponding to carbons 2 and 5 could not be placed uniquely even by least-squares fits. Two sets of binding energies gave essentially equally good fits. In one set, a 3:1 intensity pattern was used, with one unique carbon (presumably carbon 2) degenerate with carbons 4 and 6, and the other (carbon 5) at 0.4 eV higher binding energy. This is consistent both with the predictions of Davis et al[17] and with the conclusions of Clark et al.[18] In another fit (given in Table II), the "carbon 2" peak position was allowed to vary, in which case it moved out to an intermediate position. We conclude that all the

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carbon 1s peak positions are determined to a few hundredths eV except for carbon 2, which is uncertain to ± 0.13 eV. Thus with NaKα radiation it is almost possible to differentiate ortho, meta, and para carbon binding energies.

The pressure dependence of the satellites on the high binding energy side of the main peaks was not investigated. We are therefore unable to say whether they are due to energy loss or shake-up.

As our next test case, Fig. 7 shows the F1s spectrum of PF_5. This molecule has a trigonal bipyramidal structure, with the two axial bonds longer and weaker than the three equatorial bonds. The XPS spectrum taken with AlKα x-rays was reported earlier by Shaw, Carroll and Thomas.[20] Our NaKα spectrum shows a definite asymmetry on the low binding energy side, confirming the results of Shaw et al. A least-squares fit requiring two peaks with an area ratio of 3:2 gave a separation of 1.08(3) eV, in good agreement with the 1.2(1) eV value obtained earlier.[20] The linewidths were found to be 1.85(3) for the equatorial and 2.00(5) eV for the axial fluorines (Shaw et al. fixed the FWHM at 2.0 eV). When our linewidth values are considered along with the fluorine linewidths in SF_4[20] and ClF_3[20] it is seen that, in each of the three molecules, the peak corresponding to the axial fluorine(s) is broader than that due to the equatorial fluorines.[20] In this case the higher resolution available with NaKα radiation was of limited value because the lines were so wide.

We also studied the core spectrum of molecular oxygen, reported earlier by Siegbahn et al.[10] and by Bagus et al.[21] Under the constraint of equal linewidths for the quartet and doublet states, we obtained an intensity ratio of 2.51(3) with $MgK\alpha_{12}$ and 2.48(5) with $NaK\alpha_{12}$, in

excellent agreement with the experimental result of Bagus et al.[21] (2.47(3)). However, when the two linewidths were allowed to vary, the $MgK\alpha_{12}$ ratio changed to 2.16(7). (Linewidths were 0.90(5) eV and 0.78(2) eV for the $^2\Sigma^-$ and $^4\Sigma^-$ states, respectively, and the $NaK\alpha_{12}$ ratio changed to 2.3(1), with FWHM of 0.71(7) eV and 0.65(3) eV.) These results are in excellent agreement with the calculated value of 2.28.[21] We note that it is very plausible for $^4\Sigma$ and $^2\Sigma$ to have different linewidths, since the calculations of Bagus et al.[21] yield different charge distributions for the high- and low-spin hole states. This difference in charge reorganization following ionization may well result in different linewidths.[15]

V. CONCLUSIONS

Synchrotron radiation provides the ultimate in high-resolution, variable-energy photon sources for photoelectron spectroscopy, and monochromatized x-rays provide intense, high-resolution sources at fixed energies. Both incur disadvantages in terms of cost and/or accessibility; it is therefore still desirable to develop "conventional" anode sources with different materials. In this paper we have dealt with simple, low-cost yttrium and sodium anodes that can be adapted to almost any x-ray photoelectron spectrometer.

Our main conclusion is that it is feasible to obtain useful molecular structure information with a sodium anode, even under modest vacuum conditions. Observation of asymmetry in the Cls line of methane, arising from vibrational structure, is perhaps the most convincing evidence, although the m-difluorobenzene data are strongly supportive

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of this conclusion. The NaKα_{12} line is superior in terms of resolution to other high-energy characteristic line sources, although not as good as monochromatized lines. Other results that may prove widely useful are the characterization of the NaKα_{12} satellite spectrum with a neon converter and determination of np/ns intensity ratios in rare gases at YMζ and MgKα_{12} energies.

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*Work performed under the auspices of the U. S. Energy Research and Development Administration

†Present address: The University of British Columbia, Department of Chemistry, Vancouver, B.C., Canada.

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13) Compare with the magnesium values: Kα' is 5.00 eV from $K\alpha_{12}$ and 0.006 of its intensity. $K\alpha_3$ and $K\alpha_4$ are respectively 8.41 eV and 10.14 eV from $K\alpha_{12}$ with areas 0.063 and 0.030 that of $K\alpha_{12}$, respectively.

14) The 0.18 eV separation was held fixed, while the area ratio was determined empirically for a fixed separation of 0.18 eV.

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TABLE I. Valence shell p/s photoelectron intensity ratios ($\theta = 90^{\circ}$) of the rare gases at MgKα and YMζ energies.

Atom	MgKα Relative Intensity			YMζ Relative Intensity	
	This work	Siegbahn et al.[10]	Other	This work	Other
Neon	0.42(4)	0.34(2)	0.39(1)*	7.1(3)	6.3(3)*
Argon	1.87(5)	2.0(4)	1.8(1)†	5.3(2)	5.3(2)† (ZrMζ)
Krypton	3.04(5)	2.5(6)	4.7(2)†	2.1(1)	--
Xenon	--	4.0(8)	4.5(2)†	--	--

*Reference 3.

†Reference 9.

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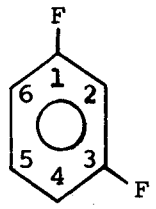
TABLE II. Comparison of carbon 1s shifts in metadifluorobenzene with theoretical CNDO potential model predictions.

	Nucleus	3:1 Fit (eV)	1:1:2 Fit (eV)	Calcd (eV)* (point charge)	Calcd (eV)* diagonal + pp' elements
	$C_{1,3}$	0.00	0.00	0.00	0.00
	C_2	-2.37(1)	-2.12(3)	-2.33	-3.01
	$C_{4,6}$		-2.46(1)	-2.39	-3.04
	C_5	-1.93(2)	-1.90(3)	-1.82	-2.26

*From ref. 17.

FIGURE CAPTIONS

Fig. 1. X-ray tube for producing the YMζ line (132.3 eV). The anode is machined at an angle of 15° and is surrounded by a grounded shield. The gaseous sample is in a direction perpendicular to the plane of the figure.

Fig. 2. The argon 3s and 3p levels with MgKα (top) and YMζ (bottom) x-rays. Counts were obtained at increments of ∿ 0.3 eV and ∿ 0.2 eV, respectively.

Fig. 3. Neon 1s spectrum taken with $NaK\alpha_{12}$ x-rays and neighboring satellites. Linewidths are: $K\alpha_{12}$ peak, 0.68(1) eV; Kα', 0.9(2) eV; $K\alpha_3$, 0.76(4) eV, and $K\alpha_4$, 0.77(5) eV.

Fig. 4. Neon 1s with $MgK\alpha_{12}$ (top) and $NaK\alpha_{12}$ (bottom) under equal spectrometer resolution ($\Delta E/E = 6 \times 10^{-4}$).

Fig. 5. Carbon 1s spectrum of methane with $NaK\alpha_{12}$ x-rays. Counts were obtained at increments of 0.13 eV. Three Lorentzians of equal FWHM were used in the fit. (The linewidth of each was determined to be 0.65(2) eV.) Derived separations are 0.43(2) eV and 0.41(7) eV, in order of increasing binding energy.

Fig. 6. The carbon 1s region of metadifluorobenzene. Counts were obtained at increments of 0.13 eV. The three peaks under the low-binding energy peak were constrained to have equal linewidths and an area ratio of 1:1:2. Binding energy values are listed in Table II.

Fig. 7. Fluorine 1s peak of PF_5. Counts were obtained at increments of 0.09 eV. The peak has an asymmetry on the low binding energy side. It was deconvoluted as two Gaussians with a fixed area ratio of 3:2. The resulting separation is 1.08(3) eV and the linewidths are: equatorial fluorines (high binding energy peaks), 1.85(3) eV; axial fluorines, 2.00(5) eV.

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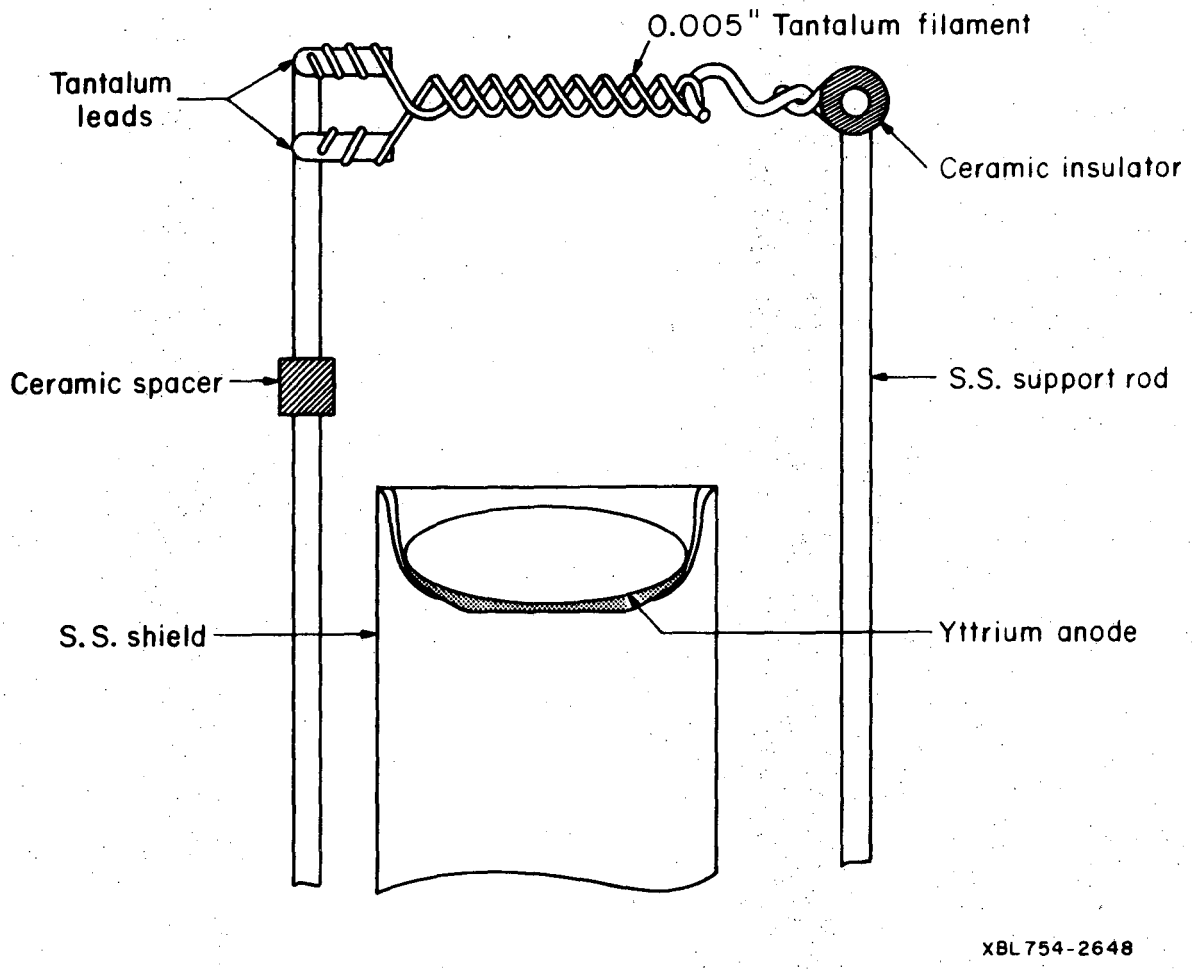

Fig. 1

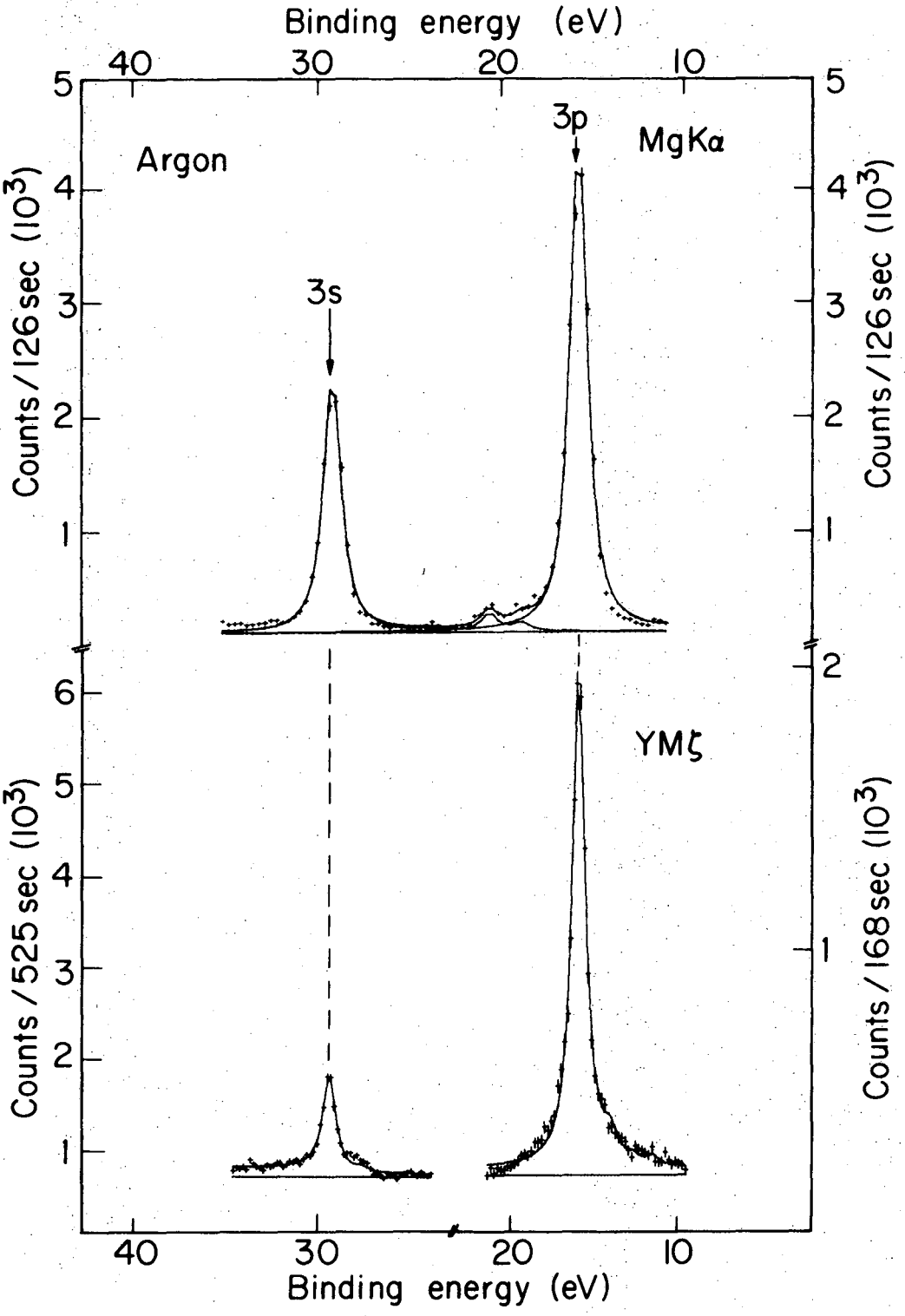

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Fig. 2

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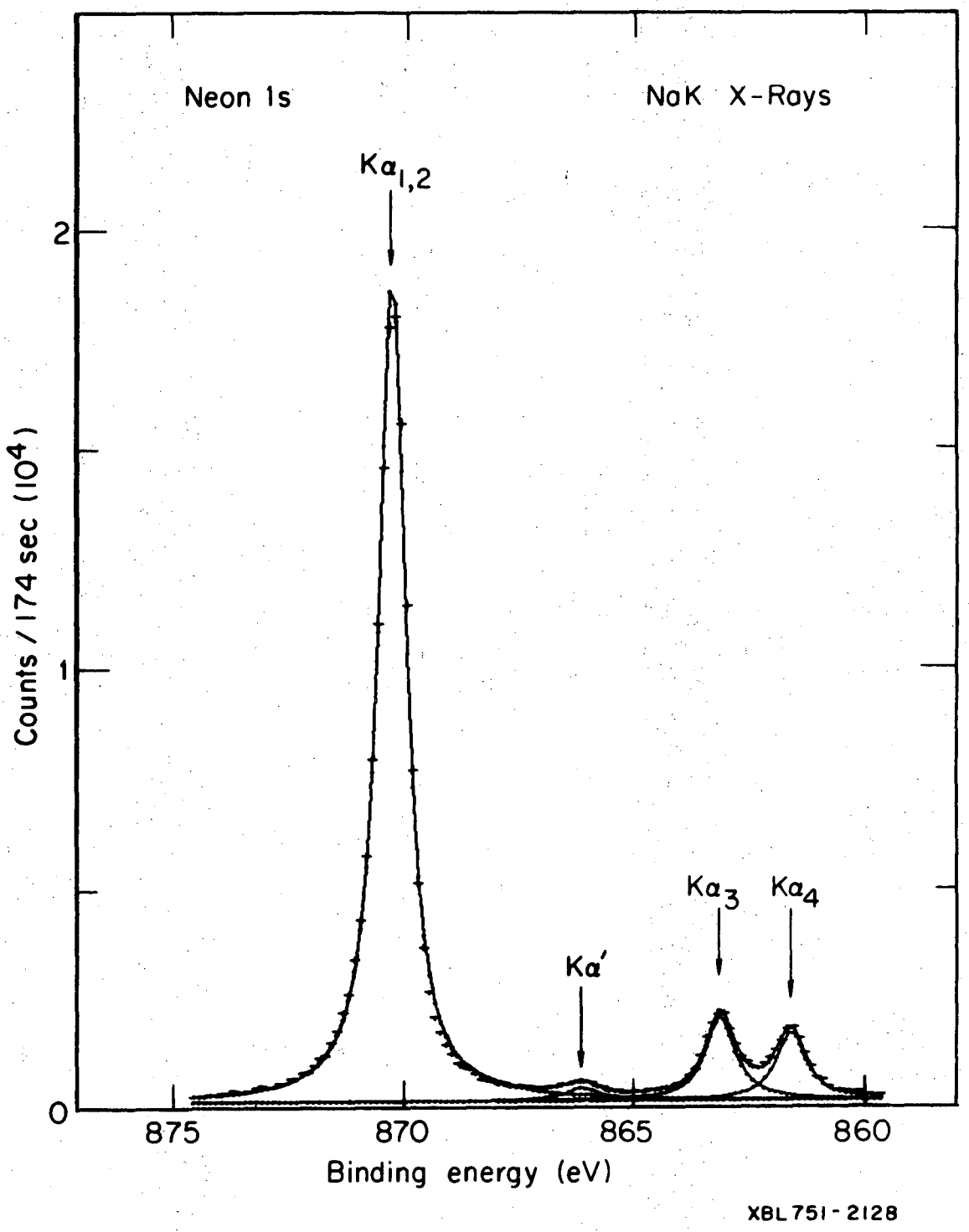

Fig. 3

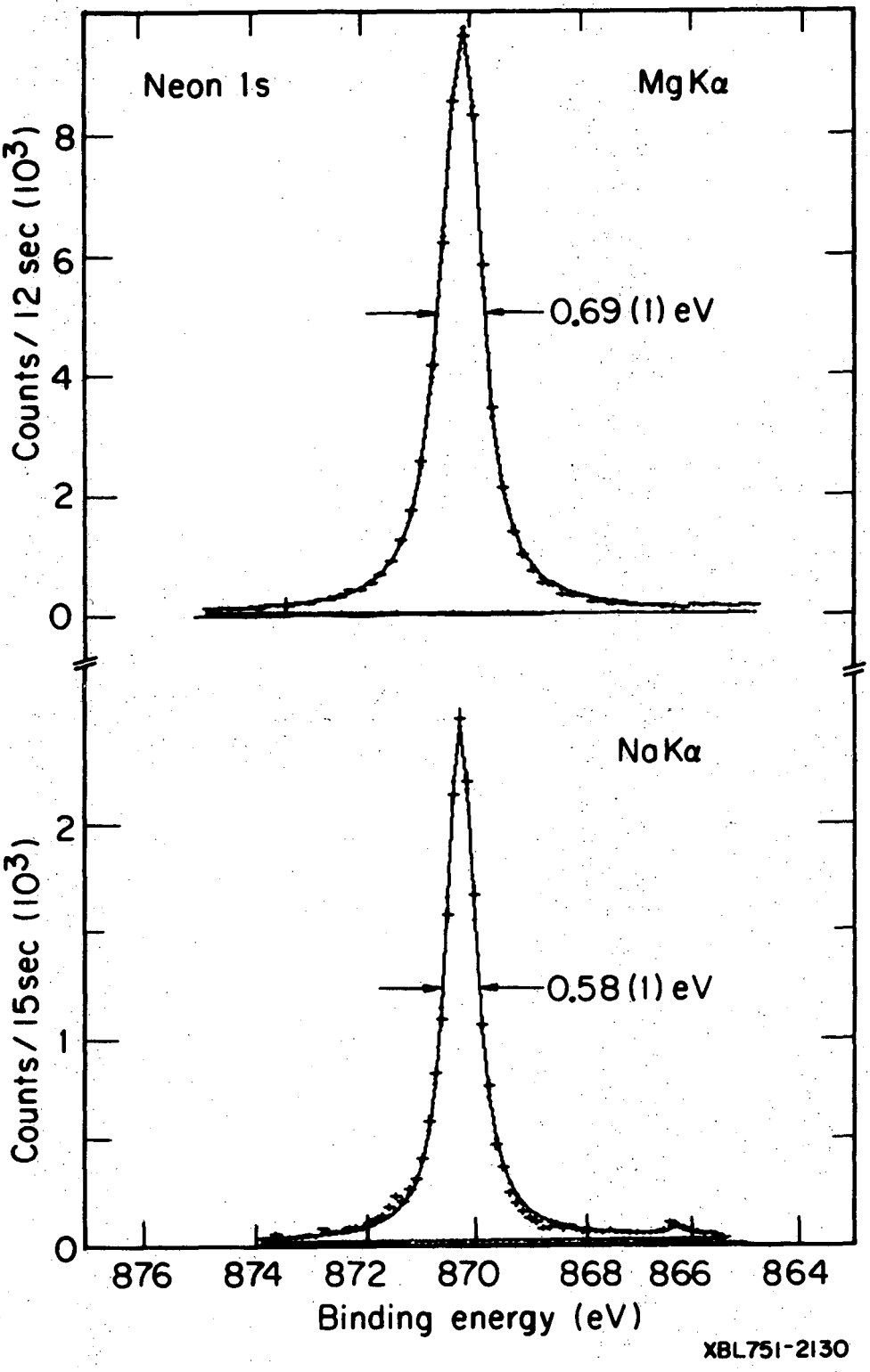
Neon 1s
Mg Kα
0.69 (1) eV
Counts / 12 sec (10³)
8
6
4
2
0
Na Kα
0.58 (1) eV
Counts / 15 sec (10³)
2
1
0
876
874
872
870
868
866
864
Binding energy (eV)
XBL751-2130

Fig. 4

0 0 0 0 4 2 0 6 2 5 2

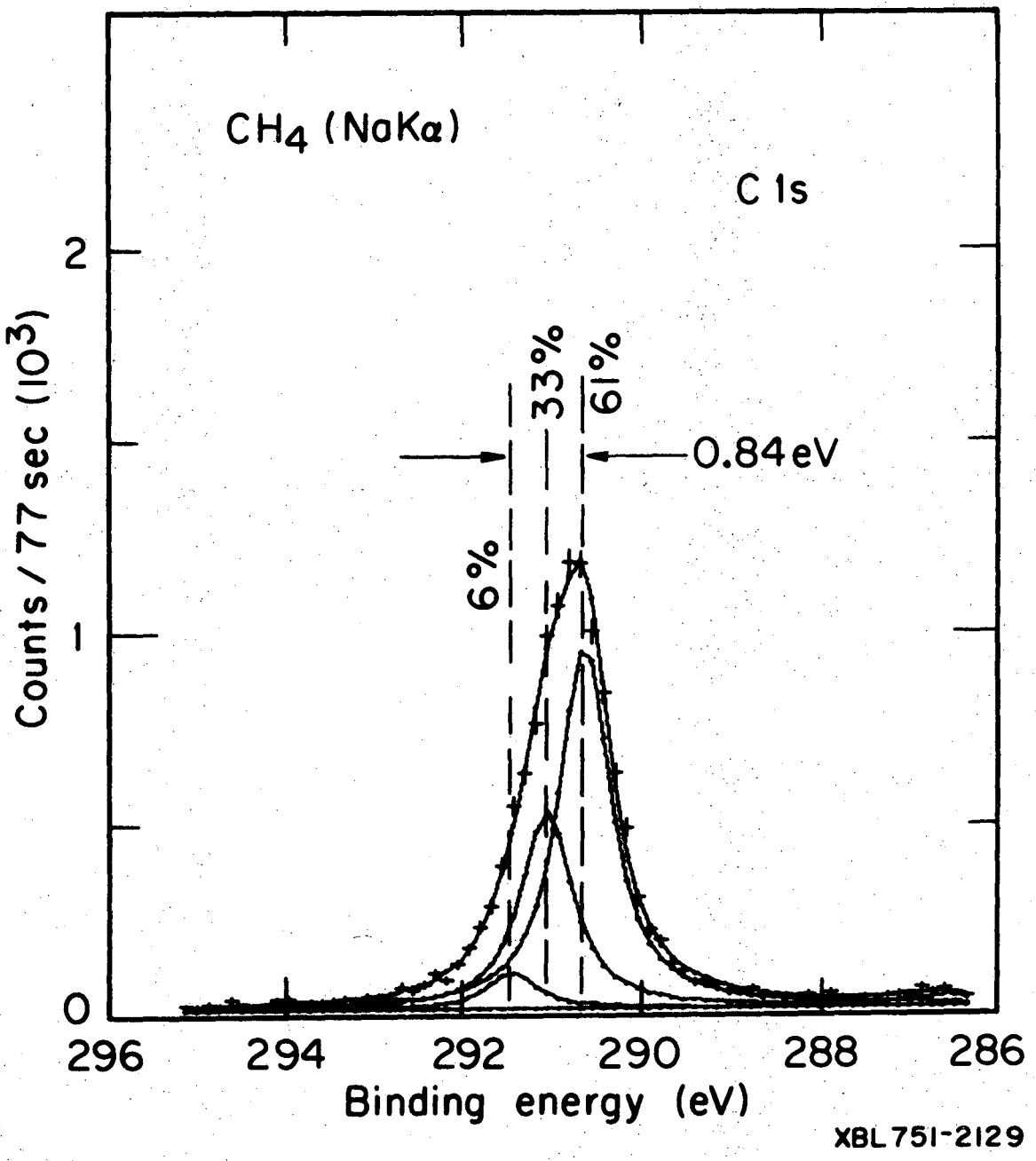

Fig. 5

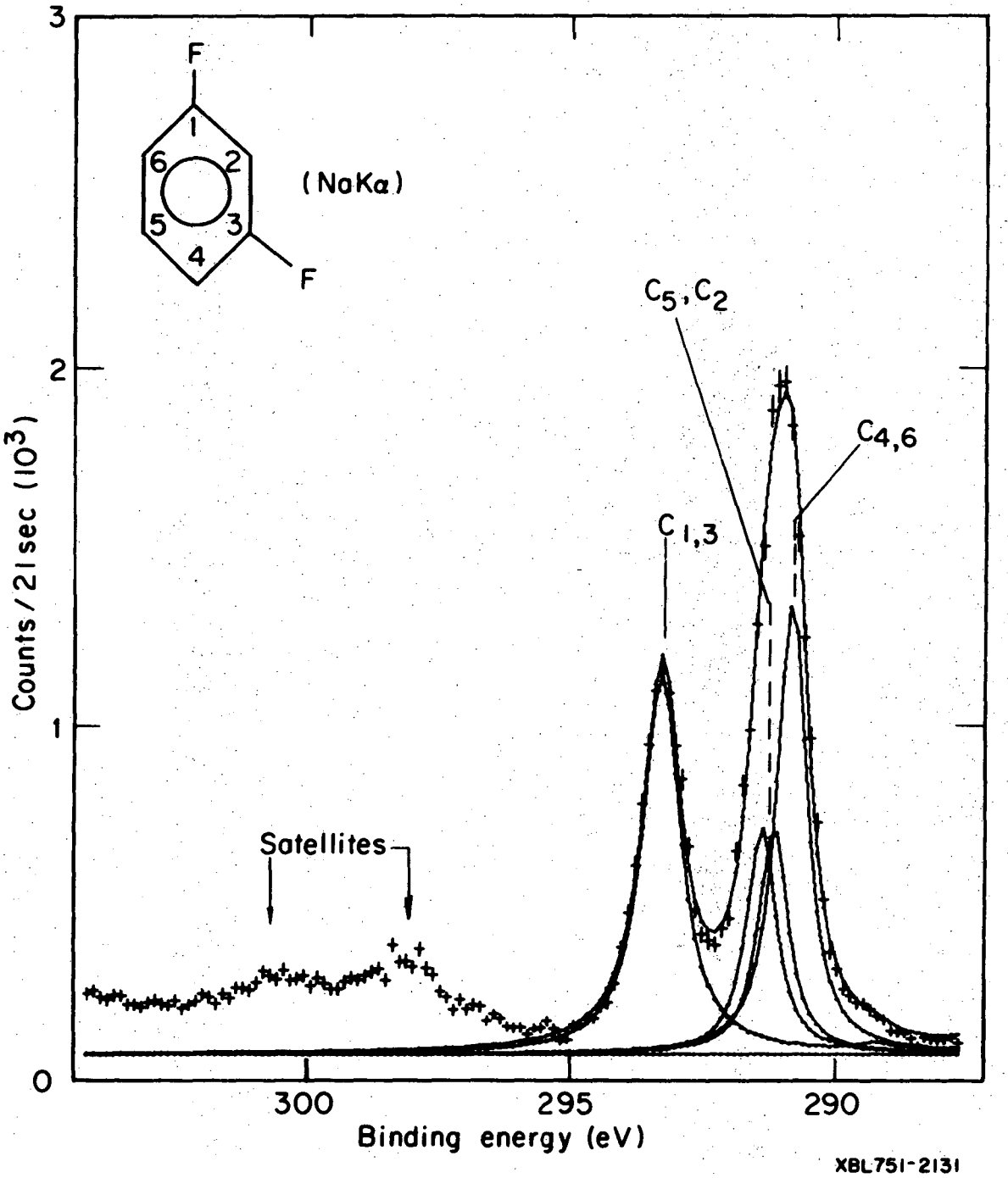
F
1
2
3
4
5
6
F
(NaKα)
C5, C2
C4,6
C1,3
Satellites
Counts / 21 sec (10^3)
0
1
2
3
300
295
290
Binding energy (eV)
XBL751-2131

Fig. 6

0 0 0 0 4 2 0 6 2 5 3

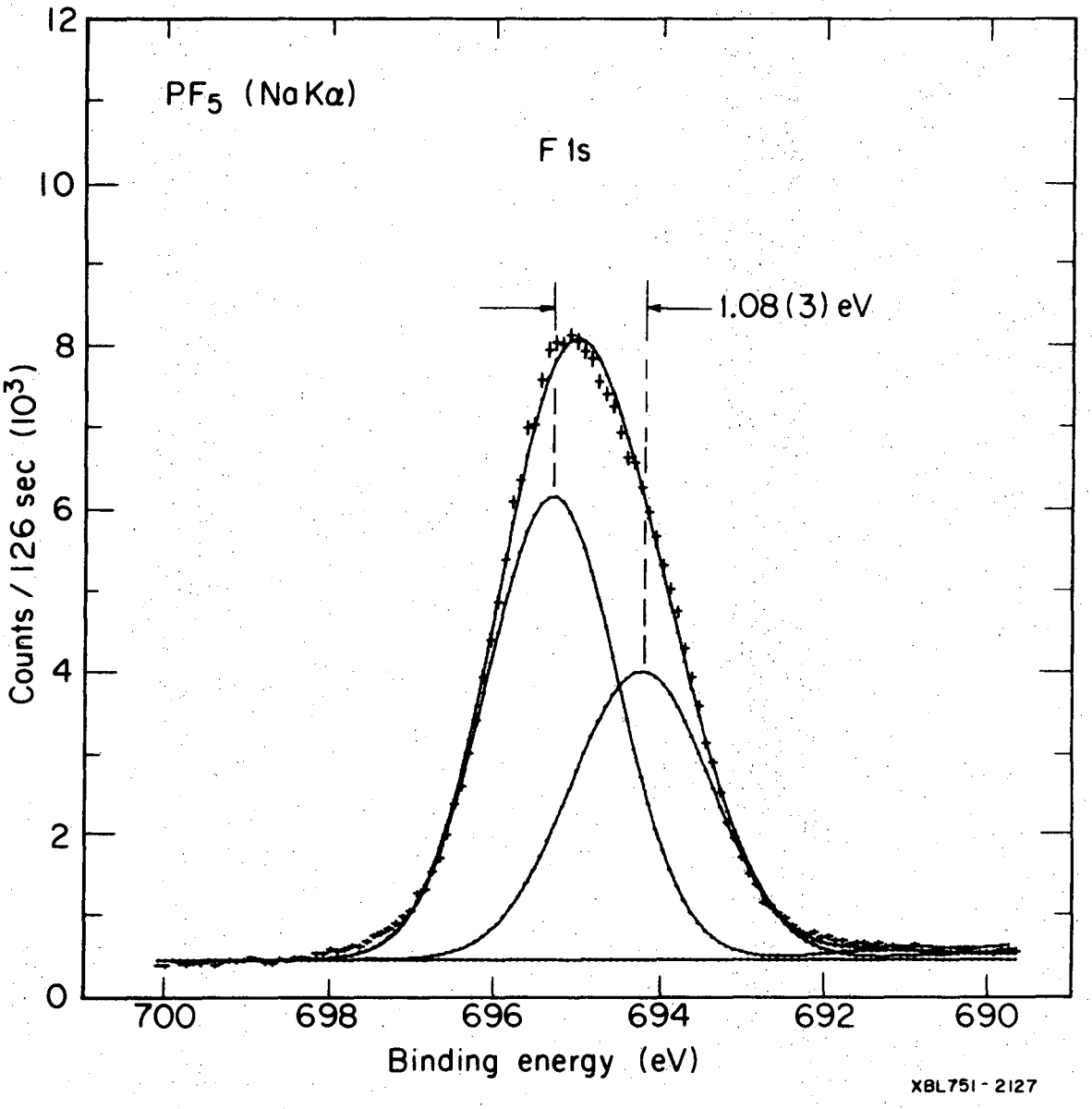

Fig. 7

0 0 0 0 4 2 0 6 2 5 4

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