High resolution, monochromatized HeIIα excited, photoelectron spectrum of the 5s correlation satellites in Xe.

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Abstract

A high resolution, monochromatized HeIIα, photoelectron spectrum of the 5s correlation satellites in Xe is presented. Approximately 70 new lines, previously not observed in photoelectron spectroscopy, were assigned using optical data. It is found that the dominating lines in the spectrum are associated with levels of high angular momentum.

Introduction

The photoelectron spectrum of Xe has been studied extensively in the past years. In 1974 Gelius [1] presented a monochromatized XPS spectrum containing a number of correlation satellite structures associated with the 5s line in Xe. These structures are due to the excitation of different final ion states resulting from electron correlation effects. The XPS spectrum has recently been improved by Svensson *et al* [2] and reveals fifteen correlation structures in the energy region between 24 and 33.5 eV binding energy. HeII excited spectra presented by Süzer and Hush [3] show eight correlation structures. A number of satellites were observed between 26.3 and 27.6 eV which could not be assigned to the J=1/2 levels of even parity used in the interpretation of the XPS spectra. Their spectrum is taken at high resolution, but with a poor signal to background ratio. Investigations using synchrotron radiation have been published by Fahlman *et al* [4] and Adam *et al* [5]. These studies are made in the region of the Cooper minimum, which occurs at about 33 eV. Synchrotron radiation studies have also be reported by Brion *et al* [6], covering 33 lines and structures in the energy region between 21.6 and 34.4 eV binding energy. Furthermore, Brion *et al* report the occurrence of one peak below the 5s peak, at 23.397 eV, and two CI states below the first single-particle shake-up state. However, satellites of low intensity were not observed. The purpose of their studies was to investigate the intensity ratio of the strong lines and the β parameter values of the satellites as functions of the photon energy. These investigations show a strong excitation energy dependence of the 5s satellite lines.

The assignments of the photoelectron spectra have mainly been made by comparison with optical energies given by Moore [7] and Hansen and Persson [8,9]. The interpretation has previously been difficult due to the fact that several states fall within the same structures in the spectrum. Also, only J=1/2, even parity satellites were considered by Hansen and Persson in their analysis of the photoelectron spectrum of Gelius [1]. Hansen and Persson have suggested that this is correct for high excitation energies where the final ionic state configuration interaction is the dominating mechanism of the 5s electron excitation. These authors also proposed that, at low excitation energies, the satellite spectrum is probably due to "ionization in the 5p shell and is associated with excitations to the $5s^2 5p^4$ 6p, 7p and possibly also with 4f final states", i.e. a conventional interpretation in terms of shake-up and conjugate shake-up.

In the present study, a new photoelectron spectrum of the 5s correlation satellites in Xe has been recorded using monochromatized HeIIα radiation. A survey spectrum is shown in figure 1, and the inner valence region is shown in greater detail in figures 2-4. The latter spectrum shows a large number of resolved lines and structures with binding energies in the region between 23.4 and 35.0 eV. Almost every line can be assigned using the optical energies given by Hansen and Persson. If this interpretation is adopted it turns out that the J=1/2, even parity states are not dominating at the excitation energy of HeIIα (40.8 eV). On the contrary, states with high J quantum numbers such as J=9/2, 7/2, 5/2 and 3/2 are seen to be present within the same range of intensities as the J = 1/2 states in the spectrum.

Experiment

The spectrum presented in this work was recorded using a dedicated gas phase photoelectron spectrometer. The instrument has been described elsewhere [10]. The exciting HeII radiation was produced by a microwave discharge ECR lamp [11]. The important feature of this lamp is that it gives a very high HeII intensity and works at much lower He pressure than conventional VUV sources. The radiation was monochromatized using a newly designed monochromator for HeII [12]. The purpose of the monochromator is to eliminate the intense HeI radiation. In combination with a system of light baffles, it also serves to reduce the background caused by scattered radiation and photoelectrons emitted from the walls of the sample cell.

The Xe gas was commercially obtained and has a purity of 99.995% . The pressure in the gas cell was held at approximately 20 mTorr. At this pressure, inelastic scattering of the electrons is negligible. The photoelectron linewidth was approximately 50 meV (FWHM). This width is mainly limited by the analyzer resolution at high pass energy (50eV) used to obtain the full spectrum within a resonable time.

The ECR lamp used in this study produces, besides the HeIIα line, a number of other radiation components [13]. Some of these components, of low intensity compared to the HeIIα line, fall withing the energy window defined by the monochromator and give rise to weak satellite structures in the spectra. One may note that even the HeIIβ line is not completely eliminated by the monochromator. The other HeII satellites lines of detectable intensity in the HeIIα region are the 320.29Å and 305.76Å lines. Furthermore, the HeIα,β,γ,δ,ε lines are still observable the spectrum. This is mainly due to diffuse scattering of the radiation at the grating.

No appreciable impurities, besides the helium gas leakage from the ECR lamp, were detected in the spectrum. A small signal resulting from excitations to the X state in the H_2O cation was detected in the 12.5 to 13.0 eV binding energy region. However, this impurity gives a negligible contribution to the 5s correlation satellite spectra above the 5s main peak.

Results and discussion

The spectrum presented in figure 2 reveals, due to its high resolution and good signal to noise, a large number of states not observed in previous photoelectron spectra of the 5s correlations satellites in Xe. The peaks of the spectrum have been analyzed by fitting gaussian line shapes. The method of analysis and the tools used have been described elsewhere [14]. The line positions, line widths, relative intensities and assignments are presented in table 1. The assignments presented in table 1 are based on the optical energies and assignments made by Hansen and Persson [9]. No assumptions as to final state symmetry or selection rules of the transitions have been made.

The resolution of the spectrum is about the same as in the earlier HeII excited spectrum [3], but the signal to noise ratio is greatly enhanced, due to higher HeII intensity, reduced scattering and a lower sample gas pressure. The main $5p_{3/2,1/2}$ lines have a line width (FWHM) of 47 meV. The line width of the 5s line is 59 meV. The signal to background is about $10^5 : 1$ in the $5p_{3/2}$ peak.

The interpretation of the correlation spectrum is rather straightforward in the region above the 5s main peak, at 23.397 eV, up to about 29.3 eV. Above this limit, a number of states fall within unresolved structures of the spectrum. In this region we have made a single gaussian fit to each structure and in table 1 we list all states that have binding energies that according to optical data fall within that particular structure.

The optical energies and assignments, made by Hansen and Persson, are supplied up to the $5s^25p^4(^3P_1)5g$ state at 32.136 eV. Therefore, no assignments have been made above this limit. However, from the spectrum it is clear that the correlation satellite states continue up to at least 35 eV. This is obvious also from the XPS given in ref. [2]. An estimation of long range variations in the relative intensities of the structures in the region above 30 eV is very uncertain, since the spectrometer transmission function is not accurately known under the conditions used when this spectrum was taken.

The dominating lines in the present spectrum are found to correspond to the final states $(^3P)6p\ ^2D_{3/2,\,5/2}$ (27.539 eV), $(^1D)5d\ ^2D_{3/2}$ (27.942 eV), $(^1D)5d\ ^2G_{9/2,\,7/2}$ (26.374 eV), $(^1D)5d\ ^2F_{5/2}$ (26.895 eV), and $(^3P)5d\ ^4P_{1/2}$ (25.265 eV), in order of decreasing intensity, *cf* Table 1. These lines were also observed in the previous spectra recorded at, or near, the HeIIα excitation energy [3,4].

According to Hansen and Persson, the transition to the $5s^25p^4(^1D)5d\ ^2S_{1/2}$ level should give rise to a strong feature at about 28.876 eV in the photoelectron spectrum due to strong interaction with the $5s5p^6\ ^2S_{1/2}$ level. In the XPS at 1487 eV this line is also dominating in the satellite region. The line is not resolved in our UPS spectrum due to overlapping lines resulting from the $5p_{3/2}$ line excited by the HeIδ line. However, it is obvious that this line is weak in the UPS spectrum, cf figure 2. Thus it seems that the higher angular momentum components of the $(^1D)5d$ configuration acquire the highest intensity in the HeII excited spectrum. This may suggest that electron correlation in the initial state plays an important role for the photoelectron intensities in this case. This possibility was discussed also by Fahlman *et al* [4].

As mentioned above, Brion *et al* have reported a number of unassigned peaks below the energy of the first single-particle shake-up state associated with 5p ionization. These peaks were found at 22.52, 23.7 and 23.95 eV. The present spectrum contains several unassigned peaks below the main 5s line. The strongest of these peaks, at 22.54 eV (cf figure 2), coincides with the peak observed by Brion *et al* . The structures observed by Brion *et al* around 23.7 and 23.95 eV, are in the present study assigned to excitations of the 5p electron, *cf* table 1.

Conclusions

The presented high resolution spectrum of the 5s correlation satellites in Xe shows a good correspondence with the optical energies given by Hansen and Persson. In this assignment it is found that transitions to ionic states with high angular momenta tend to dominate in the spectrum. To assign the states above 29.3 eV, an enlarged theoretical study of the 5p excited ion states has to be performed. In some cases, more conclusive assignments might also be made after some measurements at the higher spectrometer resolution recently obtained.

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Tables

Table 1.

Energies, intensities and assignments of peaks in the 5s-5p region of Xe.

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
1	12,137	0,047	1210	5p $_{3/2}$		12,130
2	13,443	0,047	784	5p $_{1/2}$		13,436
3	22,534	0,080	0,65			
4	22,710	0,075	0,22		w	
5	23,009	0,082	0,43			
6	23,122	0,082	0,33		w	
7	23,397	0,059	100	$5s5p^6\ ^2S_{1/2}$		23,397 [5]
8	23,658	0,094	0,21	$5s5p^6\ ^2S_{1/2}$ $(^3P)\ 6s\ ^4P_{5/2}$	305.76Å	23,661 23,669
9	23,743	0,059	0,20	$(^1D)\ 6d\ ^2D_{3/2}$	HeIIβ	23.740
10	23,851	0,059	0,48	He 1s $_{1/2}$	305.76Å	23,851
11	23,919	0,059	0,76	$(^3P)\ 6s\ ^2P_{3/2}$		23,917
12	23,958	0,059	0,52	$(^3P)\ 5d\ ^4D_{5/2}$		23,958
13	23,962	0,059	0,09	$(^3P)\ 5d\ ^4D_{7/2}$	w	23,963
14	24,038	0,071	0,58	$(^3P)\ 5d\ ^4D_{3/2}$		24,037
15	24,139	0,071	0,23	$(^3P)\ 5d\ ^4D_{1/2}$		24,139
16	24,450	0,052	0,74	$(^3P)\ 5d\ ^4F_{9/2}$		24,455
17	24,589	0,059	148	He 1s $_{1/2}$		24,587
18	24,672	0,059	2,4	$(^3P)\ 6s\ ^4P_{1/2}$		24,672
19	24,719	0,078	1,4	$(^3P)\ 5d\ 2F_{7/2}$		24,719
20	24,876	0,078	0,43	$(^3P)\ 6s\ ^4P_{3/2}$		24,876
21	25,053	0,094	0,43	$(^3P)\ 5d\ ^2P_{1/2}$		25,055
22	25,183	0,066	0,87	$(^3P)\ 5d\ ^2D_{3/2}$		25,187
23	25,265	0,059	4,0	$(^3P)\ 5d\ ^4P_{1/2}$		25,266

Table 1. Continued.

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
24	25,334	0,061	3,0	$(^3P)\ 5d\ ^4F_{5/2}$		25,331
25	25,395	0,066	1,7	$(^3P)\ 2s\ ^2P_{1/2}$		25,385
				$(^3P)\ 5d\ ^4F_{3/2}$	w	25,444
26	25,521	0,106	1,0	$(^3P)\ 5d\ ^4P_{3/2}$		25,509
				$5s5p6\ ^2S_{1/2}$	320Å	25,501
				$(^3P)\ 5d\ ^4P_{5/2}$		25,521
				$(^3P)\ 5d\ ^4F_{7/2}$		25,573
27	25,715	0,061	1,3	$(^1D)\ 6s\ ^2D_{5/2}$		25,714
28	25,937	0,071	0,70	$(^3P)\ 5d\ ^2P_{3/2}$		25,933
29	25,990	0,071	0,59	$(^3P)\ 6p\ ^4P_{3/2}$		25,991
				$(^3P)\ 6p\ ^4P_{5/2}$		26,011
30	26,105	0,059	0,70	$(^3P)\ 5d\ ^2F_{5/2}$		26,104
31	26,132	0,059	1,0	$(^1D)\ 6s\ ^2D_{3/2}$		26,131
32	26,216	0,068	0,59	$(^3P)\ 6p\ ^2D_{5/2}$		26,204
				$(^3P)\ 6p\ ^2P_{1/2}$		26,224
				$(^3P)\ 6p\ ^3D_{7/2}$		26,228
33	26,374	0,059	12	$(^3P)\ 5d\ ^2D_{5/2}$		26,357
				$(^1D)\ 5d\ ^2G_{9/2}$		26,377
				$(^1D)\ 5d\ ^2G_{7/2}$		26,378
34	26,609	0,066	2,0	$(^3P)\ 6p\ ^2P_{3/2}$		26,609
35	26,699	0,059	0,74	He $1s_{1/2}$	320 Å	26,691
36	26,895	0,061	5,9	$(^1D)\ 5d\ ^2F_{5/2}$		26,895
37	27,04	0,059	0,37	$(^3P)\ 6p\ ^4D_{1/2}$		27,060
38	27,112	0,071	0,78	$(^1D)\ 5d\ ^2F_{7/2}$		27,114
39	27,213	0,066	0,65	$(^3P)\ 6p\ ^4D_{3/2}$		27,210

Table 1. Continued.

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
40	27,414	0,073	0,85	$(^3P)\ 6p\ ^4D_{5/2}$		27,394
				$(^3P)\ 6p\ ^4S_{3/2}$		27,412
41	27,539	0,061	30	$(^1D)\ 5d\ ^2P_{3/2}$		27,513
				$(^3P)\ 6p\ ^2D_{3/2}$		27,540
				$(^1D)\ 5d\ ^2D_{5/2}$		27,542
				$(^3P)\ 6p\ ^2S_{1/2}$		27,575
42	27,877	0,059	1,1	$(^1D)\ 5d\ ^2P_{1/2}$		27,878
43	27,942	0,059	17	$(^1D)\ 5d\ ^2D_{3/2}$		27,941
44	28,107	0,061	1,0	$(^1D)\ 6p\ ^2F_{5/2}$		28,108
45	28,153	0,066	1,7	$(^1S)\ 6s\ ^2S_{1/2}$		28,155
46	28,207	0,066	3,0	$(^1D)\ 6p\ ^2P_{3/2}$		28,207
47	28,260	0,066	1,1	$(^1D)\ 6p\ ^2F_{7/2}$		28,256
48	28,488	0,071	0,83	$(^1D)\ 6p\ ^2D_{3/2}$		28,487
49	28,589	0,082	3,8	$(^1P)\ 7s\ ^4P_{5/2}$		28,560
				$(^1D)\ 6p\ ^2P_{1/2}$		28,588
50	28,735	0,066	1,2	$5p_{3/2}$	HeI ε	28,733
51	28,885	0,066	6,5	$(^1D)\ 5d\ ^2S_{1/2}$		28,876
				$5p_{3/2}$	HeI δ	28,898
52	29,062	0,064	5,0	$(^3P)\ 6d\ ^2P_{1/2}$		29,061
				$(^1S)\ 5d\ ^2D_{5/2}$		29,063
				$(^3P)\ 6d\ ^2F_{7/2}$		29,066
53	29,205	0,064	9,8	$5p_{3/2}$	HeI γ	29,202

Table 1. *Continued.*

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
54	29,371	0,066	10	(^3P) 6d $^4P_{1/2}$		29,330
				(^3P) 4f $_{9/2}$		29,360
				(^3P) 4f $_{7/2}$		29,365
				(^3P) 6d $^4D_{5/2}$		29,376
				(^3P) 7p $_{5/2}$		29,380
				(^3P) 4f $_{5/2}$		29,387
				(^3P) 7p $_{3/2}$		29,388
55	29,447	0,064	9,6	(^3P) 4f $_{3/2}$		29,426
				(^3P) 6d $^4P_{3/2}$		29,443
				(^3P) 7p $_{5/2}$		29,444
				(^3P) 7p $_{7/2}$		29,455
				(^3P) 4f $_{11/2}$		29,461
				(^3P) 4f $_{9/2}$		29,476
				(^3P) 7p $_{1/2}$		29,489
				(^3P) 4f $_{7/2}$		29,492
				(^3P) 4f $_{1/2}$		29,511
				(^3P) 4f $_{5/2}$		29,514
				(^3P) 4f $_{3/2}$		29,529
56	29,612	0,071	1,1	(^3P) 7s $^4P_{1/2}$		29,597
				(^3P) 7p $_{3/2}$		29,611
57	29,858	0,059	43	(^3P) 7s $^4P_{3/2}$		29,783
				(^3P) 7s $^2P_{1/2}$		29,851
				5p $_{3/2}$	HeI β	29,857
58	30,032	0,059	1,3	(^3P) 6d $^4F_{5/2}$		30,032
59	30,207	0,064	2,4	5p $_{1/2}$	HeI δ	30,204
60	30,348	0,061	2,1	(^3P) 6d $^2F_{5/2}$		30,347

Table 1. *Continued.*

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
61	30,424	0,066		(^3P) 4f $_{5/2}$		30,420
				(^3P) 8s $^2P_{3/2}$		30,426
				(^3P) 4f $_{7/2}$		30,426
62	30,502	0,066	9,1	(^3P) 6d $^2P_{3/2}$		30,490
				5p $_{1/2}$	HeI γ	30,508
				(^1S) 6p $^2P_{1/2}$		30,508
				(^3P) 4f $_{3/2}$		30,526
63	30,635	0,106	4,0	(^1S) 6p $^2P_{3/2}$		30,628
				(^3P) 4f $_{7/2}$		30,639
64	30,773	0,075	5,1			
65	30,910	0,118	1,5	(^2P) 5g $_{9/2}$		30,907
				(^2P) 5g $_{7/2}$		30,907
				(^2P) 5g $_{11/2}$		30,908
				(^2P) 5g $_{9/2}$		30,908
				(^2P) 5g $_{7/2}$		30,914
				(^2P) 5g $_{5/2}$		30,914
66	31,063	0,075	2,4	(^1D) 6d $^2G_{7/2}$		31,064
				(^1D) 6d $^2G_{9/2}$		31,076
67	31,166	0,064	25	5p $_{1/2}$	HeI β	31,163
				(^1D) 6d $^2P_{3/2}$		31,172
				(^1D) 6d $^2F_{5/2}$		31,172
				(^1D) 6d $^2F_{7/2}$		31,221
				(^1D) 6d $^2D_{5/2}$		31,228
68	31,302	0,080	5,1	(^1D) 6d $^2P_{1/2}$		31,271
				(^1D) 6d $^2D_{3/2}$		31,299
69	31,400	0,059	2,4	(^1D) 4f $_{3/2}$		31,405

Table 1. *Continued.*

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
70	31,45	0,059	0,43	(^3P) 6f $_{11/2}$	w	31,451
				(^3P) 6f $_{9/2}$	w	31,452
71	31,496	0,087	8,9	(^1D) 4f $_{9/2}$		31,497
				(^1D) 4f $_{5/2}$		31,501
				(^1D) 4f $_{3/2}$		31,509
72	31,61	0,059	2,2	(^3P) 8s ^4P $_{3/2}$		31,607
				(^1D) 4f $_{7/2}$		31,608
73	31,726	0,059	630	5p $_{3/2}$	HeI α	31,726
74	31,952	0,092	5,4	(^3P) 5g $_{7/2}$		31,920
				(^3P) 5g $_{9/2}$		31,920
				(^3P) 7g $_{11/2}$		31,986
				(^3P) 7g $_{13/2}$		31,988
				(^3P) 7g $_{11/2}$		31,988
75	32,211	0,106	2,1			
76	32,415	0,141	1,5			
77	32,535	0,071	1,7			
78	32,811	0,141	5,0	(^1S) 7s ^2S $_{1/2}$		
79	33,031	0,059	304	5p $_{1/2}$	HeI α	33,032
80	33,180	0,118	1,7			
81	33,440	0,118	1,3			
82	33,557	0,087	3,8			
83	33,641	0,071	2,4			
84	33,728	0,089	1,6			
85	33,892	0,089	3,8			
86	34,030	0,113	1,9			
87	34,165	0,082	0,35			

Table 1. *Continued.*

Peak Designation	Peak Energy (eV)	Peak Width (FWHM)	Relative Peak Heights [1]	Assignment [2]	Comment [3]	Energy [4]
88	34,320	0,094	1,7			
89	34,507	0,087	1,5			
90	34,577	0,047	0,39			
91	34,648	0,064	1,4			
92	34,750	0,061	0,70			
93	34,845	0,066	0,65			
94	34,910	0,064	0,65			
95	34,996	0,066	0,91			
96	35,088	0,068	0,98			

1 Normalized to 100.00 for the 5s5p6 2S1/2 peak at 23.397 eV binding energy.
2 The assignments are based on the energy levels given by Hansen and Persson [9].
3 Excitation radiation component. 'w' indicates a line of low intensity.
4 Optical energies given by Hansen and Persson [9].
5 Optical energy used for calibration.

Figures

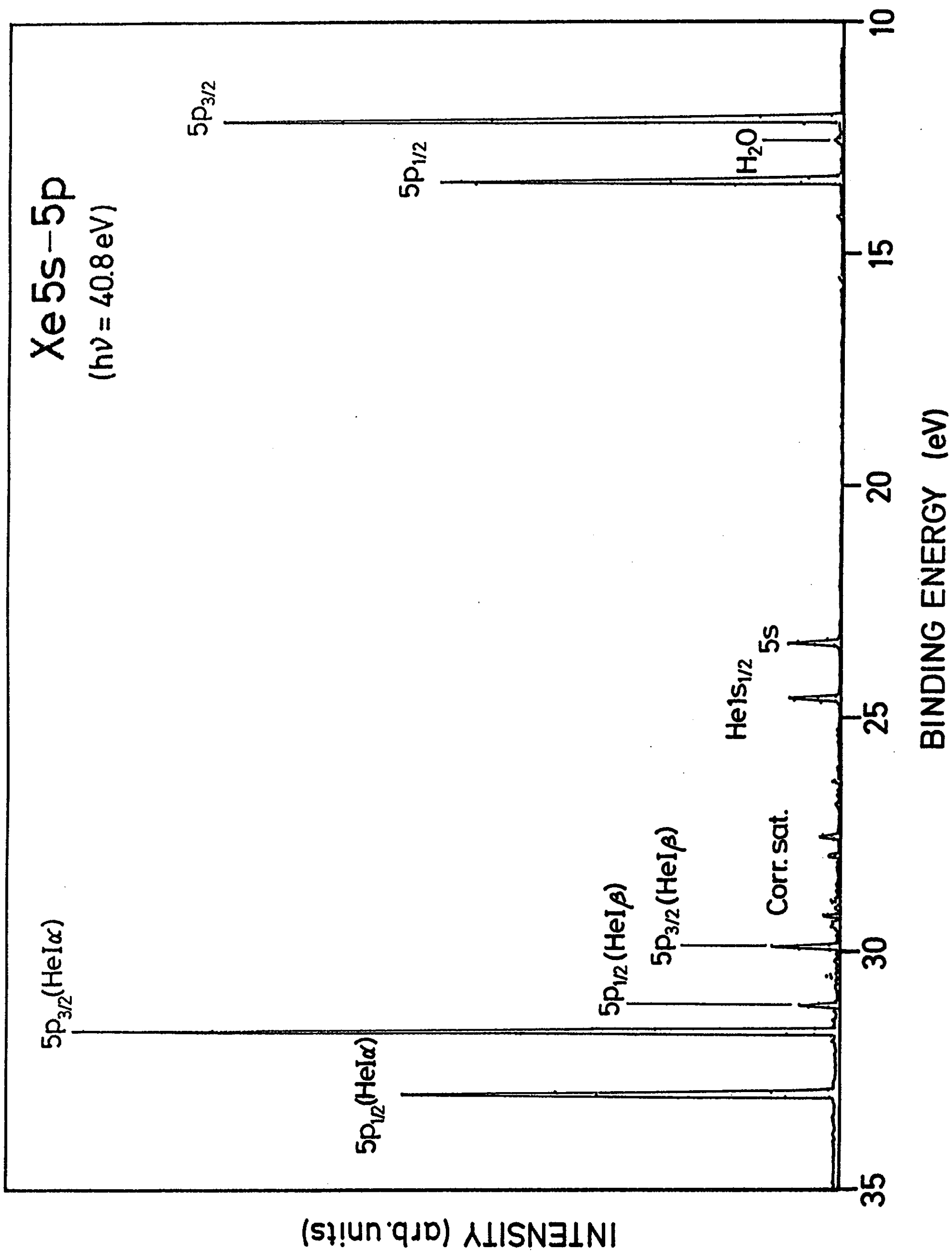

Fig. 1. *A survey high resolution photoelectron spectrum of the 5s correlation satellites in Xe. The recording time for the spectrum was approximately 15 min.*

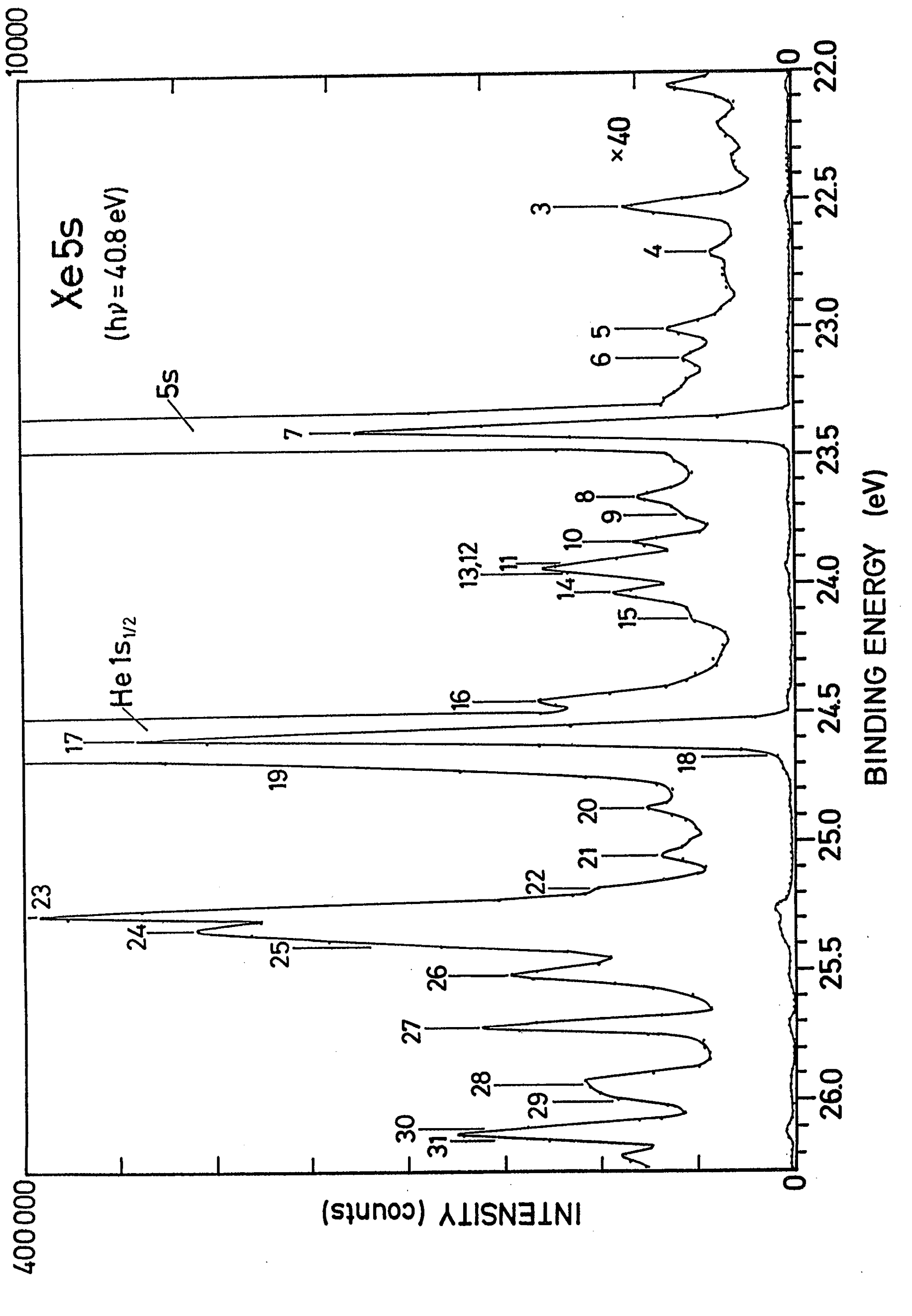

Fig. 2. *A detail of the high resolution inner valence photoelectron spectrum of Xe between 22.0 and 26.5 eV. The recording time for the whole inner valence spectrum presented in figure 2-4 was approximately 10 hours.*

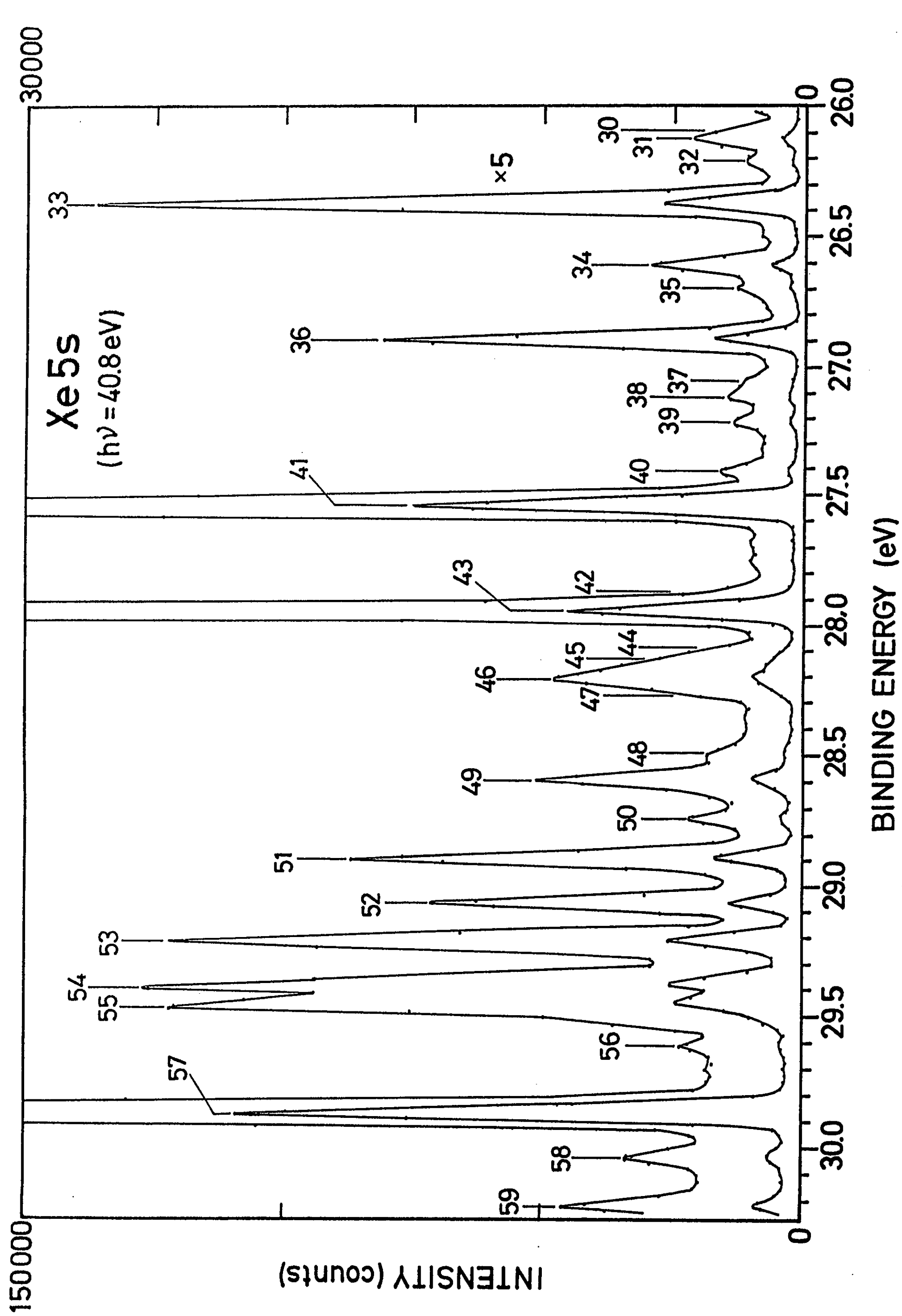

Fig. 3. *A detail of the high resolution inner valence photoelectron spectrum of Xe between 26.0 and 30.5 eV.*

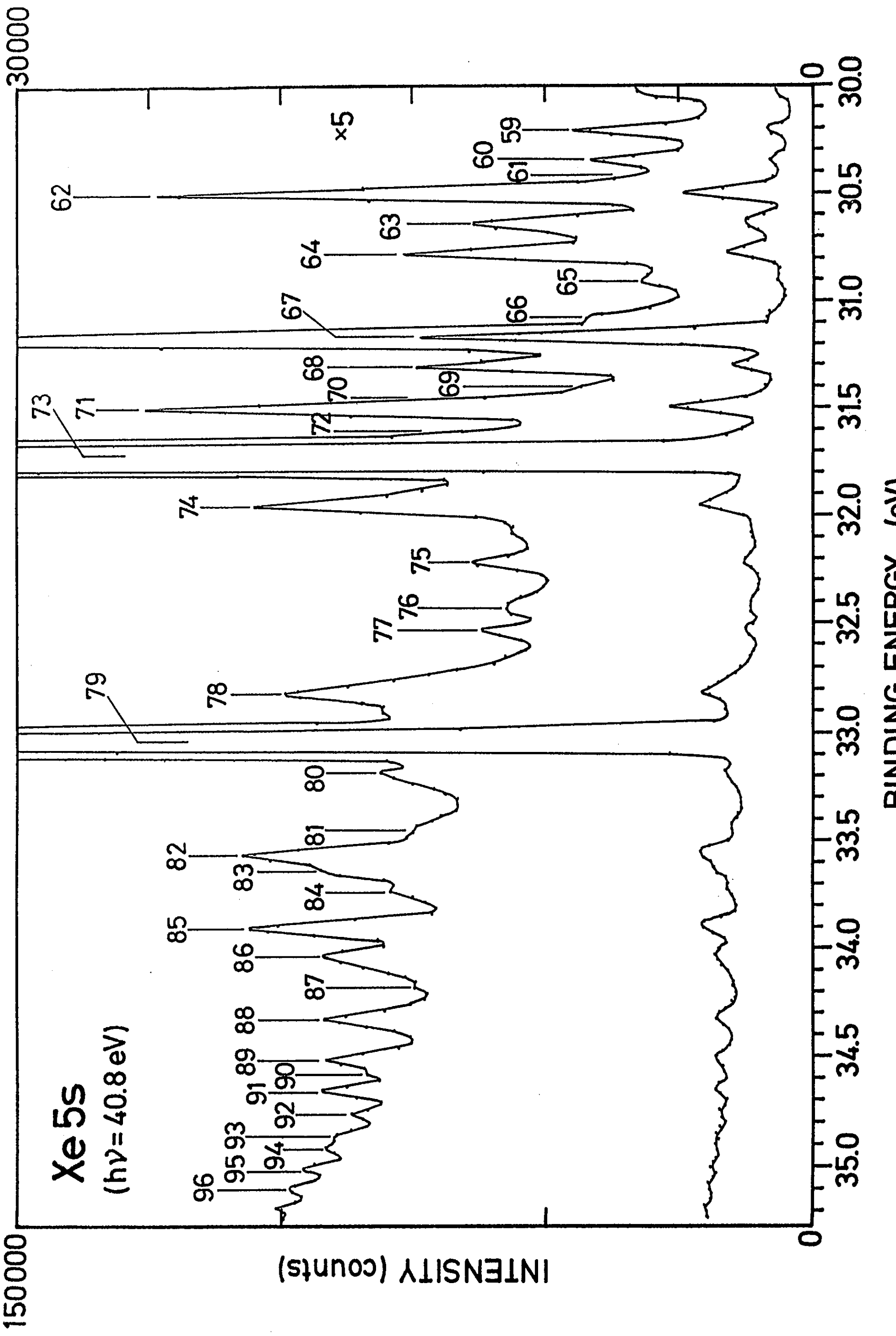

Fig. 4. *A detail of the high resolution inner valence photoelectron spectrum of Xe between 30.0 and 35.5 eV.*