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PHOTOELECTRON SPECTRA OF METAL TETRAKISMETHYLTRIHYDROBORATES AND THORIUM TETRAHYDROBORATE

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Photoelectron Spectra of Metal Tetrakismethyltrihydroborates and Thorium Tetrahydroborate

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Abstract

HeI and HeII photoelectron spectra of $M(BH_3CH_3)_4$, M = Zr, Hf, Th, and U and that of $Th(BH_4)_4$ in the vapor phase have been obtained. Assignments of the bands based on the Xα SW calculations of Hohl and Rosch (preceding paper) are given.

Photoelectron Spectra of Metal Tetrakismethyltrihydroborates and Thorium Tetrahydroborate

Introduction

The volatile metal tetrahydroborates ($M(BH_4)_4$, M=Zr, Hf, Th, Pa, U, Np, Pu), have been the subject of structural, vibrational, optical, photoelectron (PE), and theoretical studies.[1-8] For the actinide tetrahydroborates, one of the major questions has been the extent of the f orbitals involvement in the bonding in these complexes.[5,6] Unfortunately, the first three members of the actinide borohydride series, $Th(BH_4)_4$, $Pa(BH_4)_4$, and $U(BH_4)_4$ are polymeric in the solid state with a metal site symmetry much lower than the T_d symmetry found in the vapor phase.[9] Recently, the volatile compounds, $M(BH_3CH_3)_4$ where M = Zr, Th, U, and Np have been synthesized and structurally characterized.[10] These studies have shown the metal ion is at a site of approximately T_d symmetry in the solid state. Magnetic measurements for both $U(BH_3CH_3)_4$ and $Np(BH_3CH_3)_4$ have been interpreted on this basis.[11-13]

Photoelectron spectra of $Zr(BH_4)_4$, $Hf(BH_4)_4$, and $U(BH_4)_4$ have been published and discussed previously by two groups.[5,6] Quasirelativistic Xα-SW calculations of $M(BH_4)_4$ (M=Zr, Hf, Th, and U) have been described in the preceding paper and reproduced the ionization energies satisfactorily except for a uniform shift.[8] We report in this paper the photoelectron spectra of $M(BH_3CH_3)_4$ (M=Zr, Hf, Th, and U) and for completeness, $Th(BH_4)_4$. These spectra are assigned on the basis of their similarities to the $M(BH_4)_4$ compounds and the results of the Xα-SW calculations.

Experimental

Photoelectron spectra were obtained using a PES Laboratories 0078 spectrometer, with data collection either on an XY recorder or by means of a RML 380Z microprocessor. The spectra were calibrated by reference to Xe, N_2 and He. The methyltrihydroborate samples were prepared as described previously.[10] $Th(BH_4)_4$ was prepared as described by Katz and Hoekstra.[14]

Results

He I and He II spectra were obtained for $Th(BH_4)_4$ and $M(BH_3CH_3)_4$ (M = Zr, Hf, Th, and U) in the vapor phase. Ionization energy (IE) data are given in Table 1, and representative spectra shown in Figures 1-5. As most of the bands were broad and featureless, they are not well characterized by the chosen IE, and identification of trends necessitates comparison of the whole band shape and position.

The PE spectra of the thorium and uranium tetrakismethyltrihydroborates show two bands in the region 10-16 eV. $U(BH_3CH_3)_4$ has an additional band at 8.3 eV, which shows a substantial intensity increase in the He II spectrum, and may be associated with ionization of the $5f^2$ electrons. A further three high IE bands are most clearly defined in the He II spectrum (see Figure 3).

In contrast the Zr and Hf analogues have an additional low energy band with a maximum at circa 10 eV. Intensity comparisons suggest that this ionization comprises part of the first band in the spectra of the actinide tetrakismethyltrihydroborates. Otherwise the spectra are very similar to those of their heavier congeners. There is a very low intensity band at 24.7 eV visible in the He II spectrum of $Hf(BH_3CH_3)_4$. A similar band was found at 26.1 eV for $Hf(BH_4)_4$[5] and assigned to ionization of the 4f shell.

The spectrum of $Th(BH_4)_4$ shows only one band below 16 eV and two bands at higher IE. Apart from the absence of the f-band, it closely resembles the spectrum of $U(BH_4)_4$.[5]

Discussion

The spectra of $M(BH_4)_4$ where M = Zr, Hf[5,6] and U[5] have been reported previously. These two groups differ in their assignment of the lowest energy band. The spectrum of $Th(BH_4)_4$ was measured by us for completeness and as anticipated resembles that of the uranium rather than the zirconium and hafnium analogues. The main differences of the tetrakismethyltrihydroborate derivative PE spectra are the presence of extra bands at ca 14 eV and 20 eV and the shift of other bands to lower IE. Interestingly the additional low energy band found for the Zr and Hf tetrahydroborates at 11.6 eV is also present (at 10 eV) in the Zr and Hf tetrakismethyltrihydroborates. Whatever the cause of this difference between the ionization behavior of the transition metal and actinide tetrahydroborates it is not supressed by methyl substitution.

The band at ca 22 eV can be assigned to carbon 2s ionizations, and those between 16 and 20 eV to the t_2 and a_1 boron 2s ionizations.

The profile of the principal ligand bands may be illuminated by comparison with the PE spectra of methane and ethane.[15] Whereas methane shows a broad Jahn-Teller split band between 13 and 16 eV associated with the t_2 ionization, ethane has two principal bands. The first one between 11 and 14 eV comprises the $1e_g$ (π_{CH_3}-) and $3a_g$(σ_{CC}) ionizations whereas that between 14 and 16.5 eV is assigned to the $1e_u$ (π_{CH_3}+) ionization. In $BH_3CH_3^-$ it seems likely that the B-C sigma ionizations will also lie in the lower IE band. Indeed, the intensity ratio of these two bands, which is approximately 6:4, suggests that this is the case. In considering the π ionizations it is reasonable to expect that boron character will predominate in the lower IE band and carbon character in the upper of the two main bands. We therefore expect

features associated with the methyltrihydroborate complexing to be associated principally with the low energy band. The direct comparison of this band with the principal band of the tetrahydroborates is thus justified. Assignments for the observed ionization energies based on the preceding discussion and the results of Xα-SW calculations[8] are also given in Table 1.

The differences between the transition metal and actinide tetrahydroborates (and methyltrihydroborates) are worthy of comment. The principal difference is the separation of the low energy band from the main band for Zr and Hf in both the unsubstituted tetrahydroborates and methyltrihydroborates. Three possible causes suggest themselves:

1. As Zr and Hf are smaller than Th and U greater steric repulsion between the ligands could cause the t_1 level to rise. This is consistent with the assignment of Hitchcock et al.[6]

2. The mainly terminal B-H and B-C orbitals could have higher energies than the B-H-M bridging orbitals and be more differentiated in the "covalent" transition metal complexes than in the "ionic" actinide complexes. This is the assignment of Downs et al.[5]

3. Zr and Hf have no valence orbital of t_1 symmetry whereas Th and U being f-orbital elements do. This would require the assignment of the HOMO to be t_1.[6]

The Xα-SW calculations support point 3.[8] One major difference between the transition metal tetrahydroborates and the actinide tetrahydroborates is the reversal of the bonding ligand HOMO from the $1t_1$ in Zr and Hf tetrahydroborates to the $3t_2$ in the actinide tetrahydroborates. The calculations suggest this reversal is due to a weaker interaction of the $3t_2$ orbital with the d metal orbitals and a

small bonding interaction of the 5f orbitals with $1t_1$ ligand orbital for the actinide compounds. Thus the $1t_1$ orbital is lowered in energy and $3t_2$ is raised in energy leading to the single broad band observed at ~11 eV in the actinide methyltrihydroborates (~12 eV in the actinide tetrahydroborates).

ACKNOWLEDGEMENTS

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Table 1.

Ionization Energy Data for $M(BH_3CH_3)_4$, M = Zr, Hf, Th, U, and $Th(BH_4)_4$

	$Zr(BH_3CH_3)_4$	$Hf(BH_3CH_3)_4$		$Th(BH_3CH_3)_4$	$U(BH_3CH_3)_4$	$Th(BH_4)_4$
			M_{5f}		8.3	
$1t_1$[a]	10.8[b]	10.6	$3t_2$, $1t_1$	10.9	11.0	12.0
$3t_2$, $2a_1$, 1e, $2t_2$	12.6	2.5	$2a_1$, 1e, $2t_2$	11.8	11.8	13.0
	14.3[c]	14.2[c]		13.8[c]	13.9[c]	
$1t_2$	17.5	17.3	$1t_2$	16.8	16.9	17.5
$1a_1$	18.7	19.0	$1a_1$	18.2	18.3	18.5
C_{2s}	22.0	22.1	C_{2s}	22.2	22.0	
M_{4f}		24.7				

[a]Assignments for $M(BH_3CH_3)_4$, M = Zr, Hf based on calculations for $M(BH_4)_4$ (Ref. 8).

[b]All energy data in eV.

[c]Ionization energies associated with C character of the $BH_3CH_3^-$ ligand.

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Figure Captions

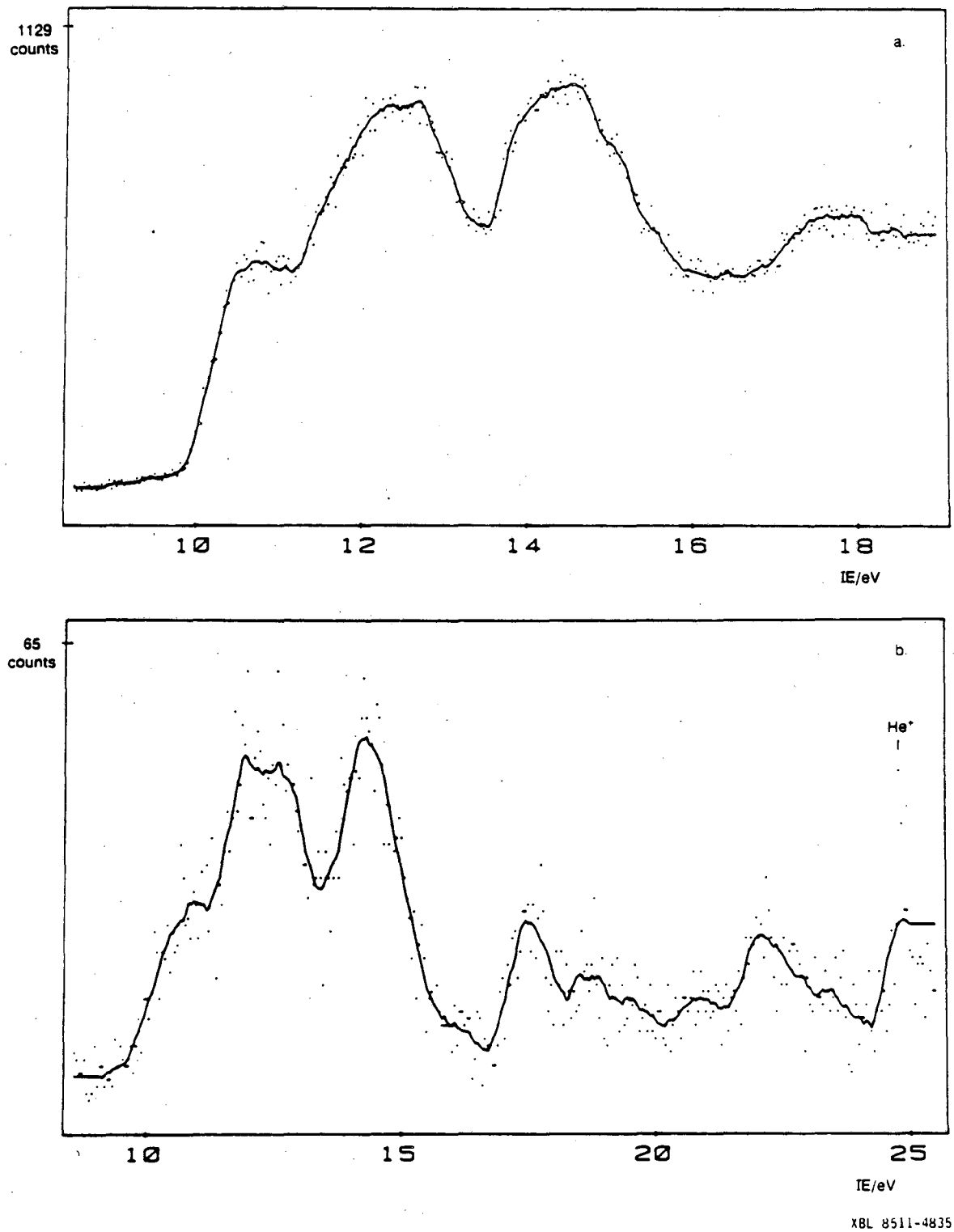
Figure 1. PE spectrum of $Zr(BH_3CH_3)_4$, a) He I b) He II.

Figure 2. PE spectrum of $Hf(BH_3CH_3)_4$, a) He I b) He II.

Figure 3. PE spectrum of $Th(BH_3CH_3)_4$, a) He I b) He II.

Figure 4. PE spectrum of $U(BH_3CH_3)_4$, a) He I b) He II.

Figure 5. PE spectrum of $Th(BH_4)_4$, a) He I b) He II.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IE/eV
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Figure 1

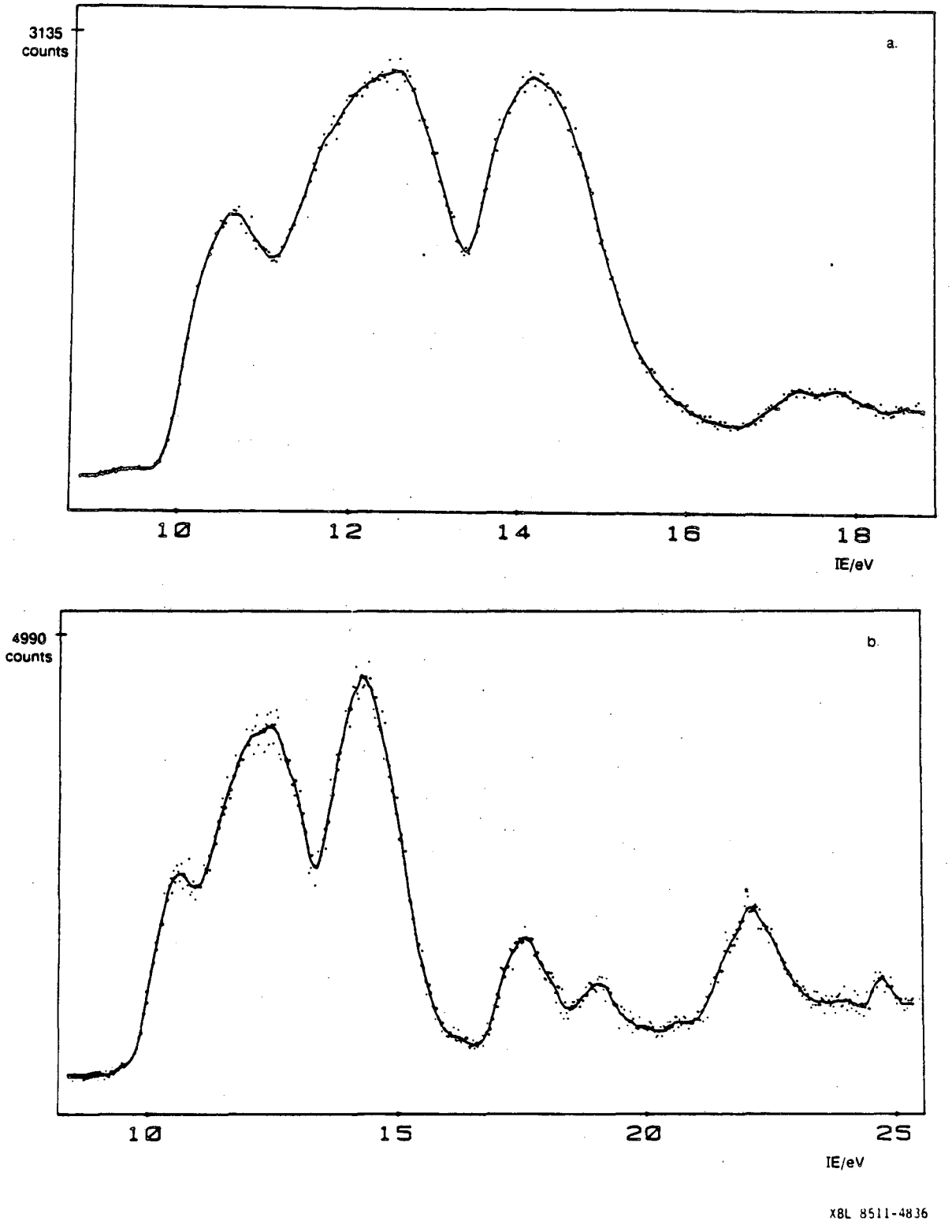
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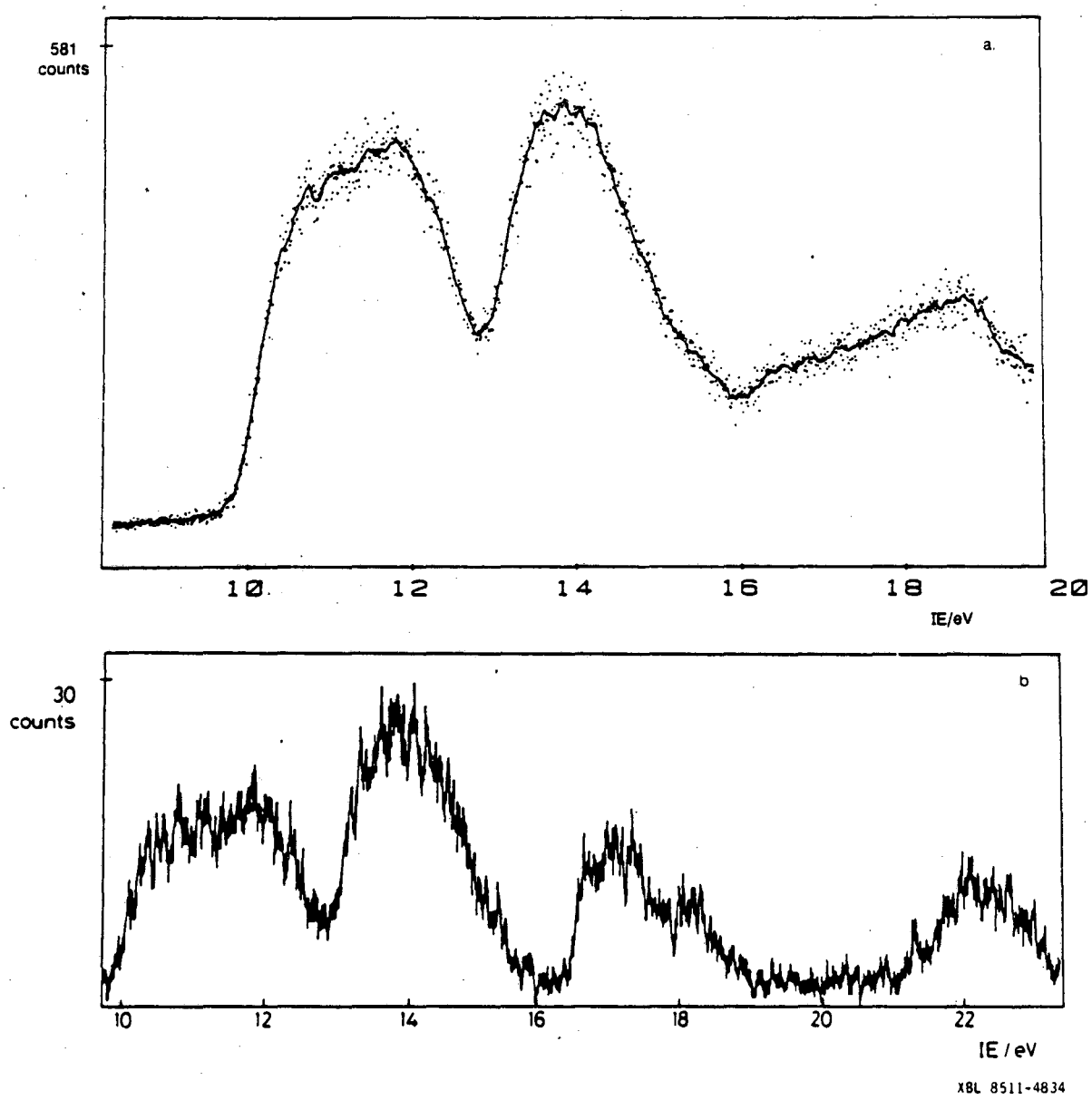
Figure 2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XBL 8511-4834

Figure 3

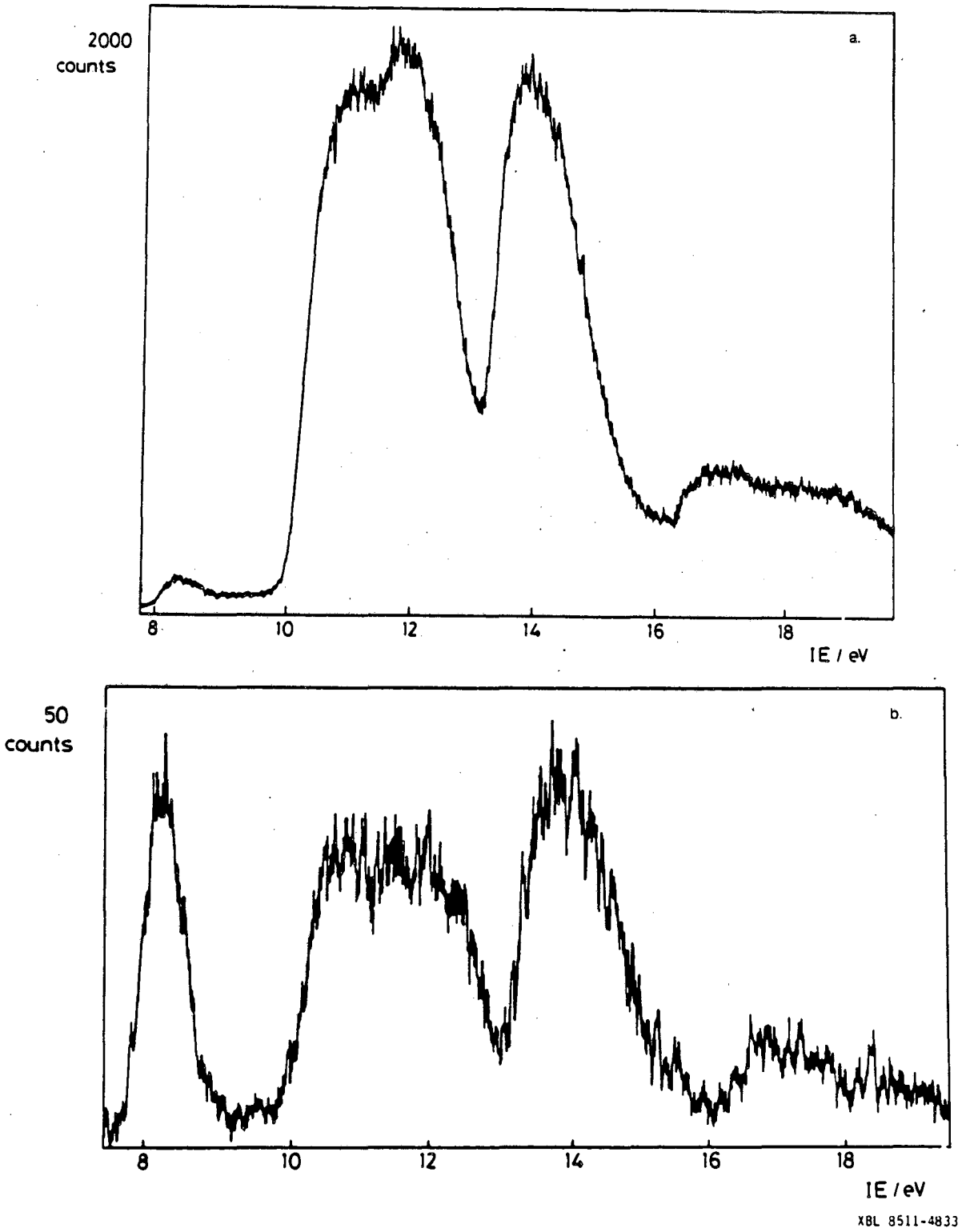
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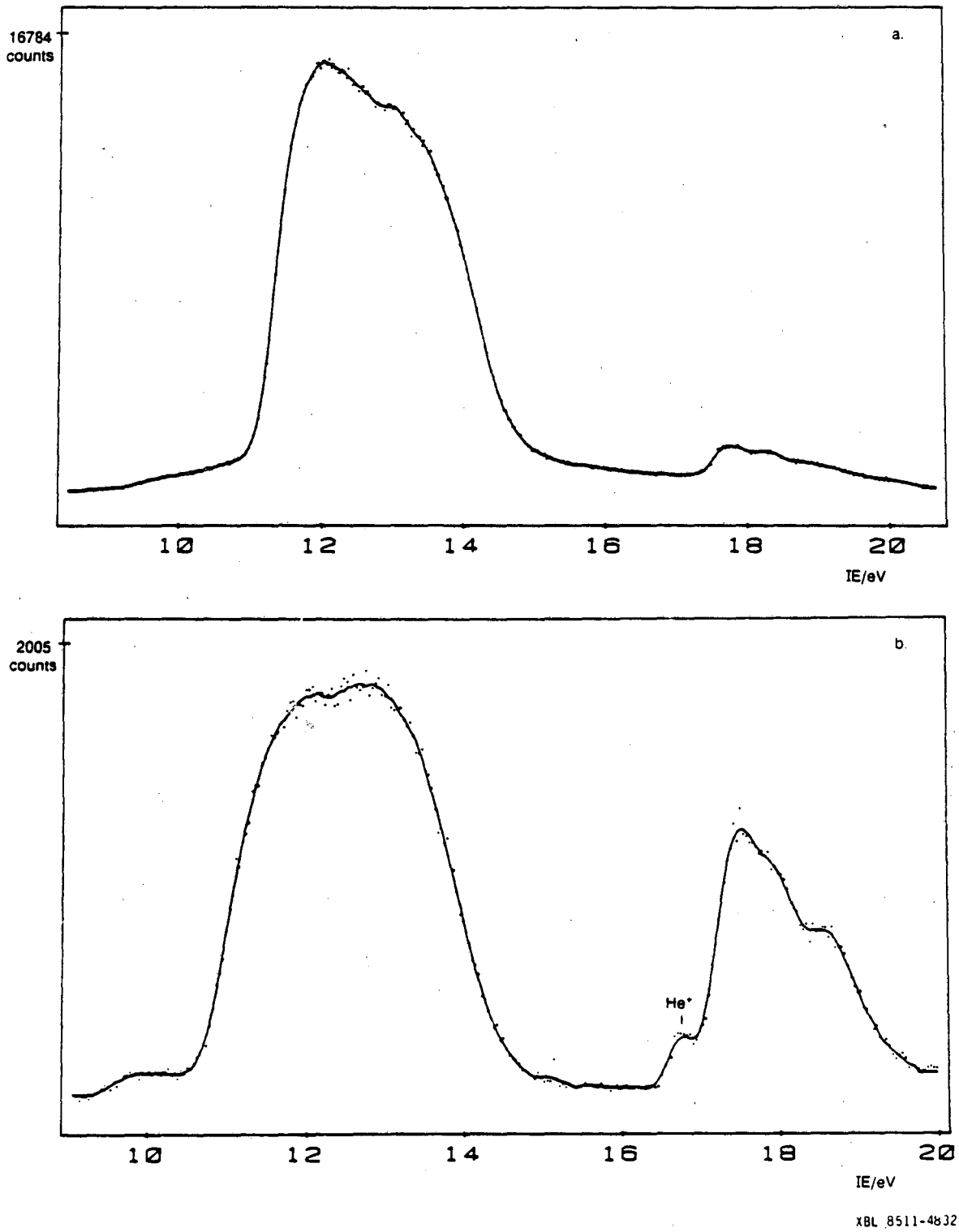
Figure 4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IE/eV
XBL 8511-4832

Figure 5

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