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VALENCE ELECTRON BINDING ENERGIES OF SOME SILICON COMPOUNDS FROM X-RAY PHOTOELECTRON SPECTROSCOPY

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ABSTRACT

X-Ray photoelectron spectra in the valence electron region were obtained for gaseous SiH_4, SiH_3CH_3, $Si(CH_3)_4$, SiH_3Cl, and SiF_4. The experimental ionization potentials and relative peak intensities are consistent with extended Hückel theory MO calculations. The data can be rationalized without assuming substantial participation of silicon d orbitals in the bonding of these compounds.

INTRODUCTION

Photoelectron spectroscopy enables one to measure molecular ionization potentials (IP's) which are lower than the energy of the ionizing photon. Koopmans' theorem[1] states that, in the absence of electronic relaxation, IP's are given by the negative of orbital energies. For valence electron IP's, which are below 50 eV, the error introduced by Koopmans' theorem seems to be less than a few electron volts. Thus calculated orbital energies for valence molecular orbitals (MO's) agree fairly well with the experimental IP's, and the ordering of the MO's taken from a photoelectron spectrum almost always agrees with that from a good *ab initio* MO calculation.[2]

Most valence electron IP's are measured using ultraviolet photoelectron spectroscopy[3] (UPS) because this method has high resolution. However, IP's from MO's of high binding energy are inaccessible in the common form of UPS, and Jahn-Teller distortions during photoemission degrade the spectra of some molecules. Although X-ray photoelectron spectroscopy[2] (XPS) has poorer resolution than UPS, the higher energy IP's can be measured, and Jahn-Teller distortions have not been observed. Also, the development of a simple method of intensity analysis[4] for XPS makes the MO assignments of the spectral bands more certain.

We have measured the gas-phase XPS valence-electron IP's for SiH_4, SiH_3CH_3, $Si(CH_3)_4$, SiH_3Cl, and SiF_4. These spectra have been

interpreted with the aid of simple extended Hückel theory (EHT) MO calculations.[5] In all cases the ordering of the MO's by the EHT calculations was consistent with spectral intensities, and there was reasonable agreement between the experimental IP's and the calculated orbital energies.

EXPERIMENTAL

Silane[6], SiH_3CH_3[7], SiH_3Cl[8], and SiF_4[9] were prepared using standard methods and purified by vacuum distillation. Practical grade $Si(CH_3)_4$ was obtained from Matheson, Coleman, and Bell Co. Infrared spectra were taken of all the compounds and compared with literature spectra to insure purity.[10]

XPS spectra were taken on the Berkeley iron-free double-focussing magnetic photoelectron spectrometer.[11] Sample pressure in the irradiation chamber was approximately 70 μ. Magnesium Kα X-rays (1253.6 eV) were used to obtain the spectra of SiH_4, SiH_3Cl, and SiF_4. Aluminum Kα X-rays (1486.6 eV) were used to obtain the spectra of SiH_3CH_3 and $Si(CH_3)_4$ because the $K\alpha_{3,4}$ satellite radiation from aluminum interfered less with the spectra of these molecules than did that from magnesium. Binding energies in this work represent vertical Franck-Condon transitions and were standardized against the neon 2s binding energy (48.42 eV). During referencing, both neon and the sample gas were present in the irradiation chamber.

CALCULATIONS

The spectra were deconvoluted to obtain band positions and intensities by least-squares fitting of data to analytical lineshapes. Lorentzian or Gaussian lineshapes are normally used to fit XPS data.[2] We have found that Lorentzian lineshapes give better fits for spectra taken with magnesium Kα X-rays, while Gaussian lineshapes give better fits when aluminum Kα X-rays are used. This observed behavior may orginate in the greater energy

separation of the aluminum $K\alpha_1$ and $K\alpha_2$ X-rays. Thus, the SiH_4, SiH_3Cl, and SiF_4 spectra were fit to Lorentzian lineshapes, and the SiH_3CH_3 and $Si(CH_3)_4$ spectra were fit to Gaussian lineshapes.

The EHT calculations utilized Hoffmann's original method.[5] The diagonal elements of the Hamiltonian matrix were orbital energies from atomic calculations by Clementi[12] rather than empirical values. The off-diagonal elements were calculated using the relation

$$H_{ij} = 0.875(H_{ii} + H_{jj})S_{ij} \tag{1}$$

Overlap integrals were calculated from Slater-type orbitals using exponents and principal quantum numbers proposed by Cusachs and Corrington.[13] The valence basis set included silicon 3d orbitals as parameterized by Corrington.[14] Partial gross populations for use in intensity analysis were calculated by Mulliken analysis.[15] Molecular geometries from the literature[16] were used in the calculations.

A semi-empirical intensity analysis has been developed for XPS valence spectra.[4] The cross section for absorption of an X-ray in the one-electron and dipole approximations is[17]

$$\sigma_{j,\varepsilon\kappa} = \frac{4\pi\alpha a_o^2}{3} h\nu |\langle \psi_j | \vec{r} | \psi_{\varepsilon\kappa} \rangle|^2 \tag{2}$$

where ψ_j is the LCAO-MO from which the photoelectron is ionized and $\psi_{\varepsilon\kappa}$ is the photoelectron wave function. After expanding ψ_j in terms of atomic orbitals (AO's), the total cross section for absorption may be approximated as a sum of atomic subshell photoionization cross sections.[4] Each subshell cross section, $\sigma_{A\lambda}^{AO}$, involves a valence AO wavefunction and

the plane wave photoelectron wavefunction. For a given subshell (s, p, d, ...) of a given element, $\sigma^{AO}_{A\lambda}$ is a constant, independent of any particular molecular orbital.[4] Thus, the intensities of two valence electron bands in a spectrum are related as follows:

$$I_i^{MO}/I_j^{MO} = (\sum_{A\lambda} P_{A\lambda i}\sigma^{AO}_{A\lambda})/(\sum_{A\lambda} P_{A\lambda j}\sigma^{AO}_{A\lambda}) \qquad (3)$$

where $P_{A\lambda i}$ are partial gross populations and the index A runs over the atoms while the index λ runs over the valence atomic subshells. Although calculable in principle, relative values of the $\sigma^{AO}_{A\lambda}$ are usually determined empirically using spectra from simple molecules and partial gross populations from <u>ab initio</u> MO calculations. These quantities may then be used to predict intensity ratios for the spectra of other molecules. For hydrogen, σ_{H1s} has been found to be essentially zero,[4] thus simplifying the intensity analysis of hydrides.

Relative intensities are quantitatively given by Equation 3 if the necessary $\sigma^{AO}_{A\lambda}$ are known and the $P_{A\lambda i}$ are taken from an <u>ab initio</u> calculation.[4] For most of the molecules discussed in this paper, populations from <u>ab initio</u> calculations are not available, and we have instead used EHT populations. Because EHT calculations for heteroatomic molecules are excessively polarized, Equation 3 cannot be used quantitatively. Nevertheless, we have found that the qualitative use of intensity analysis is a powerful tool in evaluating the MO orderings given by our EHT calculations.

Silicon 3d orbitals were included in our EHT basis sets, but for our choice of parameters,[14] the d orbitals did not mix appreciably into the

filled MO's. Thus, the EHT orbital energies and AO populations and parentages which we report correspond essentially to s, p valence basis set calculations, and we shall not consider $p\pi \rightarrow d\pi$ bonding in interpreting the spectra. In addition, σ_{Si3d} is expected to be small relative to σ_{Si3s} and σ_{Si3p} because the overlap integral between the Si3d orbitals and the photoelectron would be small.[18] Therefore the d orbitals are expected to have little effect on spectral intensities.

RESULTS

Silane. The spectrum of SiH_4, shown in Figure 1, consists of two well-separated bands. In the valence electron nomenclature which we shall use in this paper, these are the $(1a_1)^2$ and $(1t_2)^6$ MO's.* The valence IP's, relative intensities of the bands, and the EHT results are listed in Table 1. Although the EHT orbital energies are about 1.6eV higher than the experimental IP's (because Koopmans' theorem neglects electronic relaxation), the energy difference between the two MO's is close to the experimental value. An extended basis set *ab initio* calculation for SiH_4 has been made by Rothenberg, Young, and Schaefer.[19] They calculated valence orbital energies of -19.89 and -13.22 eV for the $1a_1$ and $1t_2$ valence MO's, respectively. The simple EHT results are close to those from the *ab initio* calculation, and both sets of energies indicate the magnitude of error associated with the calculation of valence IP's from ground state orbital energies.

Both the $1a_1$ and $1t_2$ MO's are bonding orbitals. The $1a_1$ MO is constructed from the Si3s and H1s AO's, while the $1t_2$ MO's are constructed from Si3p and H1s AO's. The ratio of the cross sections, $\sigma_{Si3s}/\sigma_{Si3p}$, was

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* These MO's correspond to the $3a_1$ and $2t_2$ MO's from an *ab initio* calculation.

Table 1

EXPERIMENTAL AND EHT RESULTS FOR SiH_4

Orbital	IP (eV)*	ε_{EHT} (eV)	Relative Areas*	Main AO† Components
$1a_1$	18.02(5)	-19.25	1.00(7)	Si 3s
$1t_2$	12.67(7)	-14.30	.65(7)	Si 3p

* Error in last significant figure appears parenthetically.

† Hydrogen parentage is omitted.

calculated to be 2.7 using the experimental peak intensities, partial gross populations from the ab initio calculation, and equation 3. Using EHT populations, this ratio was calculated to be 2.8. Although the close agreement of the two ratios is probably fortuitous, it supports the use of EHT populations and orbital parentages for qualitative intensity analysis.

Methylsilane. The spectrum of SiH_3CH_3, shown in Figure 2, was deconvoluted into five bands. In order of decreasing binding energy, these were assigned to the $(1a_1)^2$ $(2a_1)^2(1e)^4(2e)^4(3a_1)^2$ valence MO's on the basis of the EHT calculation. The experimental and calculated data for SiH_3CH_3 appear in Table 2. The IP's were reproduced fairly well by the EHT orbital energies. The $1a_1$ and $2a_1$ MO's are carbon-hydrogen and silicon-hydrogen bonding MO's, respectively; their parentages are largely C2s plus H1s and Si3s plus H1s, respectively. The 1e and 2e MO's are also carbon-hydrogen and silicon-hydrogen bonding orbitals, but involve the C2p and Si3p AO's, respectively, rather than the s orbitals. The $3a_1$ MO is constructed from both C2p and Si3p AO's and provides most of the carbon-silicon bonding.

The SiH_3CH_3 IP's are related to those of CH_4 and SiH_4. The $1a_1$ and 1e MO's of SiH_3CH_3 give IP's at nearly the same energy as the $1a_1$ and $1t_2$ valence MO's of CH_4.[20] The $2a_1$ and 2e MO's of SiH_3CH_3 likewise give IP's of nearly the same energy as the $1a_1$ and $1t_2$ MO's of SiH_4. There is, of course, no analog of the $3a_1$ MO of SiH_3CH_3 in the MO's of CH_4 or SiH_4.

Liskow and Schaefer[21] have made an extended basis set ab initio calculation for SiH_3CH_3 which produced the same order for the valence MO's

Table 2

EXPERIMENTAL AND EHT RESULTS FOR SiH_3CH_3

Orbital	IP (eV)*	ε_{EHT} (eV)	Relative* Areas	Main AO† Components
$1a_1$	22.8(1)	-23.22	.66(3)	C 2s
$2a_1$	17.49(6)	-18.59	1.00(3)	Si 3s
1e	13.1(6)	-15.88	.06(2)	C 2p
2e	12.1(1)	-14.07	.28(2)	Si 3p
$3a_1$	11.0(3)	-12.67	.13(2)	C 2p, Si 3p

* Error in last significant figure appears parenthetically.

† Hydrogen parentage is omitted.

as was obtained from the EHT calculation. The ab initio valence MO orbital energies are (in eV): $1a_1$: -25.75; $2a_1$: -19.00; 1e: -15.34; 2e: -12.72; $3a_1$: -12.34. These energies are in somewhat poorer agreement with experiment than the EHT results.

The relative intensities of the peaks in the SiH_3CH_3 spectrum provide additional support for the EHT orbital assignment. Our data indicate that $\sigma_{Si3s}/\sigma_{Si3p} = 2.7$ while Gelius[4] found that $\sigma_{C2s}/\sigma_{C2p} = 13$; thus, s-type valence MO's for carbon and silicon should be more intense than p-type MO's. From this conclusion, one assigns the two peaks at high binding energy to the $1a_1$ and $2a_1$ MO's. On the basis of this assignment, the ratio $\sigma_{C2s}/\sigma_{Si3s}$ is estimated to be 0.3 using the relative peak intensities and EHT populations for $1a_1$ and $2a_1$ MO's. This value, however, only represents a lower limit, because the EHT populations are too polarized in favor of carbon. The correct value is probably near unity. Because the value for σ_{C2p} is quite small, the least intense peak should correspond to the 1e MO's. The 2e and $3a_1$ MO's both have considerable Si3p character. However, the bond from the doubly degenerate 2e MO's would be more intense than that from the non-degenerate $3a_1$ MO. Thus, intensity data confirm the orbital ordering given by the ab initio and EHT calculations.

Tetramethylsilane. There are sixteen filled valence MO's in $Si(CH_3)_4$. The EHT calculation yields the assignment

$$(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(1t_1)^6(3t_2)^6,$$

with binding energies ranging from 12 to 24 eV. Because of the close spacing of the levels, the spectrum, shown in Figure 3, was obtained using

one-half the usual channel width. The EHT orbital energies are in fair agreement with IP's from the deconvoluted spectrum. These data for $Si(CH_3)_4$ are presented in Table 3. The $1a_1$ MO is constructed primarily from C2s and Si3s AO's. The $1t_2$ MO's are carbon-hydrogen bonding MO's constructed from C2s and H1s AO's. The EHT energies for these MO's are fairly close to experiment. The $2a_1$ MO is constructed from the Si3s AO with additional contributions from the C2p and H1s AO's. The $2t_2$, 1e, and $1t_1$ MO's are primarily carbon-hydrogen bonding MO's, although the $2t_2$ MO's include some Si3p parentage. The EHT binding energies for these levels are more closely spaced than those obtained from the spectrum. The $3t_2$ MO's are carbon-silicon bonding MO's of mainly C2p and Si3p parentage.

A UPS spectrum of the five low-energy IP's of $Si(CH_3)_4$, showing considerable Jahn-Teller distortion, has been published;[22] the MO's were assigned using a CNDO/2[23] calculation. Considerable evidence for d orbital bonding was found by this calculation,* with the result that the CNDO/2 MO's have a different order than the EHT MO's. However, the intensities from our spectrum are consistent with the EHT assignments and not with the reported CNDO/2 assignments. As in the case of SiH_3CH_3, the s-type peaks should be significantly more intense than the p-type peaks. The largest peak represents ionization from the triply degenerate $1t_2$ MO's which are largely constructed from C2s AO's. The $1a_1$ and $2a_1$ MO's are then assigned

* We made a CNDO/2 calculation for the simpler, related molecule SiH_3CH_3 using standard Santry and Segal parameters,[23] which include 3d orbitals on silicon. The MO assignments were $1a_1$, 1e, $2a_1$, 2e, $3a_1$. These differ from the *ab initio* assignments,[21] and are inconsistent with our spectral intensities.

Table 3

EXPERIMENTAL AND EHT RESULTS FOR $Si(CH_3)_4$

Orbital	IP (eV)*	ε_{EHT} (eV)	Relative Areas*	Main AO† Components
$1a_1$	24.0(1)	-23.88	.26(2)	C 2s, Si 3s
$1t_2$	21.72(5)	-22.87	1.00(1)	C 2s
$2a_1$	15.5(1)	-16.71	.29(1)	Si 3s, C 2p
$2t_2$	14.1(1)	-16.32	.10(1)	C 2p, Si 3p
1e	13.2(4)	-15.78	.03(1)	C 2p
$1t_1$	11.5(4)	-15.10	.03(1)	C 2p
$3t_2$	10.4(1)	-11.97	.17(1)	C 2p, Si 3p

* Error in last significant figure appears parenthetically.

† Hydrogen parentage is omitted.

to the 24.0 and 15.5 eV peaks, respectively. The $2t_2$ and $3t_2$ MO's, which include Si3p AO parentage, should give more intense peaks than the 1e and $1t_1$ MO's which include only C2p and H1s AO's. Furthermore, the Si3p AO population in the $3t_2$ MO's is significantly greater than that in the $2t_2$ MO's, and thus the peak from the former would be larger. Peaks from the 1e and $1t_1$ MO's should both be weak, as was the 1e MO peak in SiH_3CH_3. Except for some ambiguity for the 1e and $1t_1$ MO's, if the spectrum is assigned on the basis of these intensity criteria alone, the EHT assignment is duplicated.

Silyl Chloride. The EHT calculation for SiH_3Cl ordered the valence MO's $(1a_1)^2(2a_1)^2(1e)^4(3a_1)^2(2e)^4$. The photoelectron spectrum of SiH_3Cl was deconvoluted into five peaks, and is illustrated in Figure 4. The experimental and calculated data appear in Table 4. The $1a_1$ MO is calculated to be nearly a pure Cl3s AO and may be considered to be nearly a chlorine lone pair orbital. The $2a_1$ MO is principally constructed from Si3s and H1s AO's and contributes silicon-hydrogen bonding to the SiH_3 group. The remaining orbitals, the 1e, $3a_1$, and 2e MO's, do not include appreciable parentage from the chlorine or silicon 3s AO's. The 1e and $3a_1$ MO's include significant Si3p, Cl3p, and H1s AO parentage. The 2e MO's although they do not have much Si3p character, are constructed from both the Cl3p and H1s AO's. This fact suggests that the description of these orbitals as chlorine lone pair orbitals[24,25] is an oversimplification. The EHT calculation may be interpreted as distributing the p-like chlorine lone pair orbitals among the 2e and $3a_1$ MO's. Also, results from the calculation are consistent with pure p silicon-chlorine bonding and s, p hybridized silicon-hydrogen bonding.

Table 4

EXPERIMENTAL AND EHT RESULTS FOR SiH_3Cl

Orbital	IP (eV)*	ε_{EHT} (eV)	Relative Areas*	Main AO† Components
$1a_1$	23.7(1)	-29.58	1.00(18)	Cl 3s
$2a_1$	17.97(9)	-18.63	.65(16)	Si 3s
1e	13.8(2)	-14.85	.64(15)	Cl 3p, Si 3p
$3a_1$	12.9(3)	-13.71	.34(15)	Cl 3p, Si 3p
2e	11.51(8)	-13.12	.72(8)	Cl 3p

* Error in last significant figure appears parenthetically.

† Hydrogen parentage is omitted.

Except for the $1a_1$ MO, the EHT orbital energies are in good agreement with the experimental values. The $1a_1$ MO is predicted to have a binding energy several electron volts higher than was observed. This error is probably caused by faulty parameterization. The Cl3s orbital energy, as calculated by Clementi[12] and used in our EHT program, is several electron volts more negative than an empirical value.[26] Because the $1a_1$ MO of SiH_3Cl given by the EHT calculation is essentially just the Cl3s AO, the predicted binding energy for this MO might also be expected to be high. Our XPS IP's for SiH_3Cl are in fair agreement with values for the four low energy IP's reported in earlier UPS studies of this compound.[24, 25]

Intensity analysis again supports the EHT assignment. The most intense peak is assigned to the Cl3s-like $1a_1$ MO. Because the cross section ratio for argon is low[4] ($\sigma_{Ar3s}/\sigma_{Ar3p} = 1.4$), one might expect that bands from MO's including Cl3p AO's would be nearly as intense as those from s-type MO's. Thus, the 17.97 eV peak is assigned to the $2a_1$ MO mainly on the basis of the energy considerations mentioned previously. The intensities of the three remaining peaks closely reflect their respective orbital degeneracies. The slightly greater intensity of the band from the 2e MO's compared to that from the 1e MO's suggests that the ratio $\sigma_{Cl3p}/\sigma_{Si3p}$ is greater than one. A corresponding example[4] is known for first row elements where $\sigma_{F2p}/\sigma_{C2p} = 1.5$.

<u>Silicon Tetrafluoride</u>. The spectrum of SiF_4, shown in Figure 5, was deconvoluted into seven bands. The EHT calculation yielded the MO sequence $(1a_1)^2(1t_2)^6(2a_1)^2(2t_2)^6(1e)^4(3t_2)^6(1t_1)^6$. Numerical data for SiF_4 appear in Table 5. The binding energies taken from the EHT calculation are in good

agreement with the experimental values. The $1a_1$ and $1t_2$ MO's are largely constructed from F2s AO's. The $1a_1$ MO does however include some Si3s AO parentage, while the parentage of the $1t_2$ MO's is almost purely F2s. The parentage of the $2a_1$ MO, although largely F2p, includes appreciable Si3s character. The $2t_2$ MO's, although largely constructed from F2p AO's, include some Si3p and a little F2s parentage. The $3t_2$ MO's include both F2p and Si3p parentage while the 1e and $1t_1$ MO's are constructed entirely from F2p AO's.

The intensities of the spectral bands are consistent with the EHT MO assignments. The two high binding energy s-like bands are most intense. The band assigned to the $2a_1$ MO is less intense than the pure s-bands, but more intense than would be expected for a pure p-band arising from a non-degenerate MO. The higher intensity of the band from the $2t_2$ MO's compared to bands assigned to the $3t_2$ and $1t_1$ MO's is consistent with the inclusion of F2s parentage in the $2t_2$ MO's. The band assigned the p-like 1e MO's has, as expected, the least intensity, and the $3t_2$ MO's, which includes Si3p parentage, give a more intense band than the pure F2p $1t_1$ MO's. (If $\sigma_{C2s}/\sigma_{Si3s} \cong 1$, then one calculates[4] that $\sigma_{F2p}/\sigma_{Si3p} \cong 0.6$.)

The XPS valence spectrum for CF_4 has been published,[2] and is qualitatively very similar to our SiF_4 spectra. The SiF_4 IP's are not as well separated as those of CF_4, but this behavior is expected when silicon is substituted for carbon. An <u>ab initio</u> calculation for CF_4[2, 4] found the same orbital assignments as our EHT calculation found for SiF_4. The CF_4 assignments, later confirmed by rigorous intensity analysis,[4] and the similarity of the CF_4 and SiF_4 spectra support the EHT assignments for SiF_4.

Table 5

EXPERIMENTAL AND EHT RESULTS FOR SiF_4

Orbital	IP (eV)*	ε_{EHT} (eV)	Relative Areas*	Main AO Components
$1a_1$	40.6(2)	-43.70	.60(9)	F 2s, Si 3s
$1t_2$	39.27(9)	-42.66	1.00(10)	F 2s
$2a_1$	21.4(2)	-21.97	.12(8)	Si 3s, F 2p
$2t_2$	19.4(2)	-21.19	.17(6)	F 2p, Si 3p, F 2s
1e	18.1(4)	-19.86	.09(6)	F 2p
$3t_2$	17.4(3)	-19.16	.13(6)	F 2p, Si 3p
$1t_1$	16.4(2)	-18.19	.11(3)	F 2p

* Error in last significant figure appears parenthetically.

The four lowest IP's of SiF_4 have previously been measured in UPS studies of the compound,[22, 27] and there is good agreement between the XPS and the UPS binding energies. In their study, Bassett and Lloyd[27] propose the same MO assignments for the spectral bands as do we. However, in a later study, Jonas, et al. propose alternate assignments based upon a CNDO/2 MO calculation which included silicon 3d orbitals in the basis set. These latter assignments, which rely upon the stabilization of some MO's by the Si3d AO's, suggest a spectrum which is inconsistent with the observed XPS intensities.

CONCLUSIONS

A summary of the binding energies from the spectra and the EHT calculations is presented in Figure 6. In this figure, the EHT orbital energies have been adjusted by an additive constant so that the calculated value of the lowest IP matches experiment. This simple adjustment takes some account of electronic relaxation, at least to the extent that the relaxation energies for all the MO's of a given molecule have the same value. The agreement between experimental and calculated values is good and compares well with ab initio and other SCF correlations.[28] It thus appears that EHT can accurately reproduce the ordering of the MO's in small and symmetric molecules such as those studied in this work, and that valence IP's may be estimated with some confidence from EHT orbital energies. Others[28, 29] have observed that, for less symmetric molecules, EHT calculations may incorrectly order groups of closely-spaced orbitals. (Some hint of this

possibility is seen in the $Si(CH_3)_4$ results, where the orbital energies for the related $2t_2$, 1e, and $1t_1$ MO's are too closely spaced.) However, even in such cases, the predicted binding energies are within a few electron volts of the experimental values.

The successful correlation of our EHT results with the spectra suggests that the main features of the chemical bonding in these compounds may be described without recourse to silicon 3d AO's. If d orbitals make important contributions to the parentage of some MO's, then the energies of these MO's should be stabilized sufficiently by $p\pi \rightarrow d\pi$ bonding to affect the order of the MO's. This was not observed: the MO orderings from the EHT calculations, which had no significant d orbital bonding, matched orderings obtained from the relative band intensities of the spectra. If d orbitals were less important, but still not negligible, the MO ordering might not be affected, but certain MO's would be energetically stabilized relative to the others. The 1e MO's in SiF_4[22] and the 1e MO's in SiH_3CH_3 are specific examples of such MO's. However, comparison of the calculated and experimental IP's (Figure 6) for SiF_4 and for SiH_3CH_3 does not indicate such stabilization. However, valence MO binding energies calculated using Koopmans' theorem may differ from measured energies by several electron volts. Thus small differences between experimental and calculated values, or the lack of small differences, may not be significant, and their interpretation in terms of d orbital bonding[25,27,30] is of dubious value. We thus conclude that, although we cannot quantify the extent of d orbital bonding in these compounds, we believe it to be small, and that the principal features of the spectra (band assignments, approximate IP's and relative band intensities) may

be rationalized by considering only s and p orbital bonding.

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FIGURE CAPTIONS

Figure 1. Valence spectrum of SiH_4. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg $K\alpha_{3,4}$ satellite radiation.

Figure 2. Valence spectrum of SiH_3CH_3. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Al $K\alpha_{3,4}$ satellite radiation.

Figure 3. Valence spectrum of $Si(CH_3)_4$. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Al $K\alpha_{3,4}$ satellite radiation.

Figure 4. Valence spectrum of SiH_3Cl. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg $K\alpha_{3,4}$ satellite radiation.

Figure 5. Valence spectrum of SiF_4. The curve through the points is the sum of the individual bands. The unlabelled bands are due to Mg $K\alpha_{3,4}$ satellite radiation.

Figure 6. Experimental and calculated valence electron binding energies for SiH_4, SiH_3CH_3, $Si(CH_3)_4$, SiH_3Cl, and SiF_4.

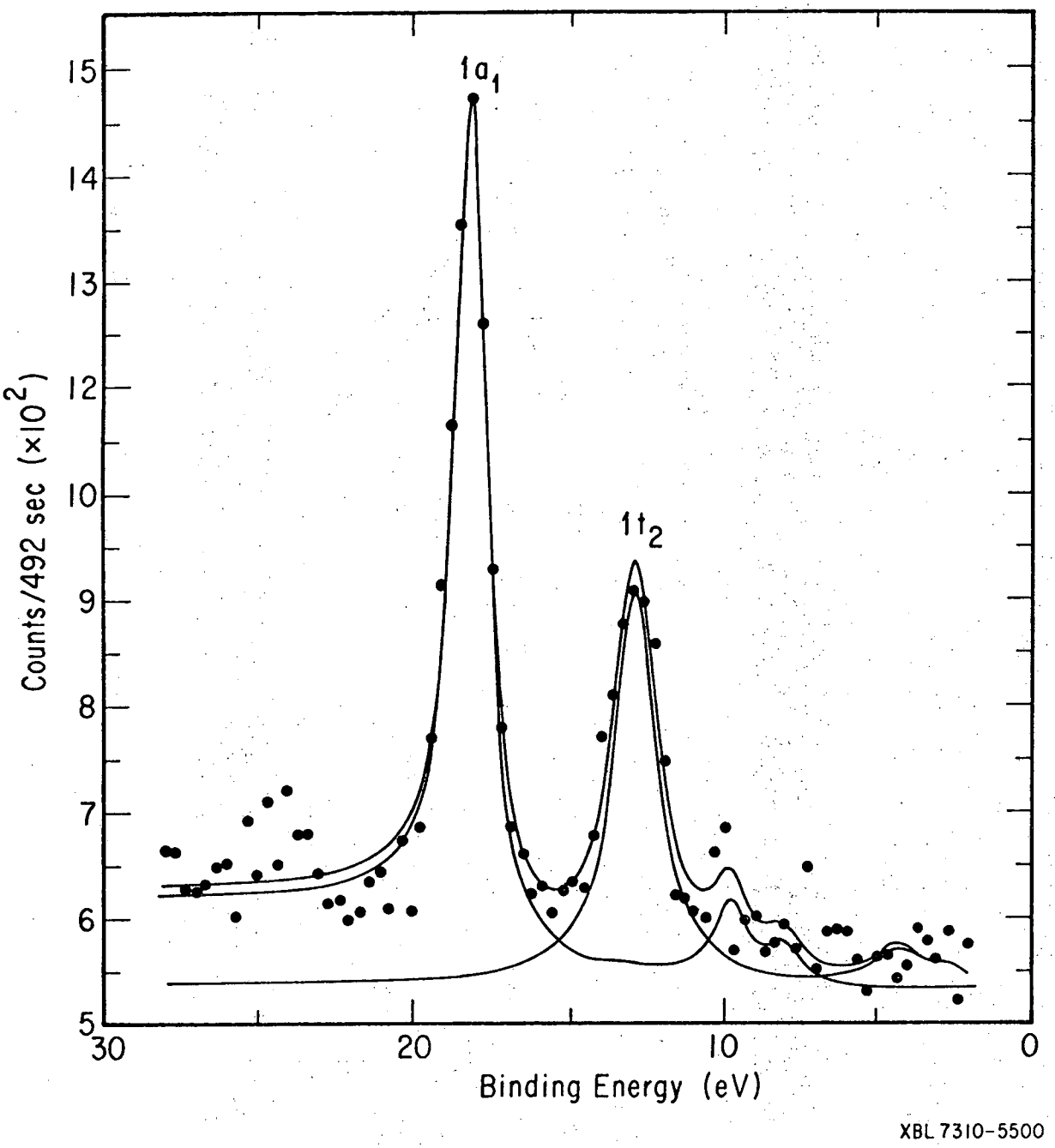
1a1
1t2
Counts/492 sec (×10²)
15
14
13
12
10
9
8
7
6
5
30
20
10
0
Binding Energy (eV)
XBL 7310-5500

Fig. 1

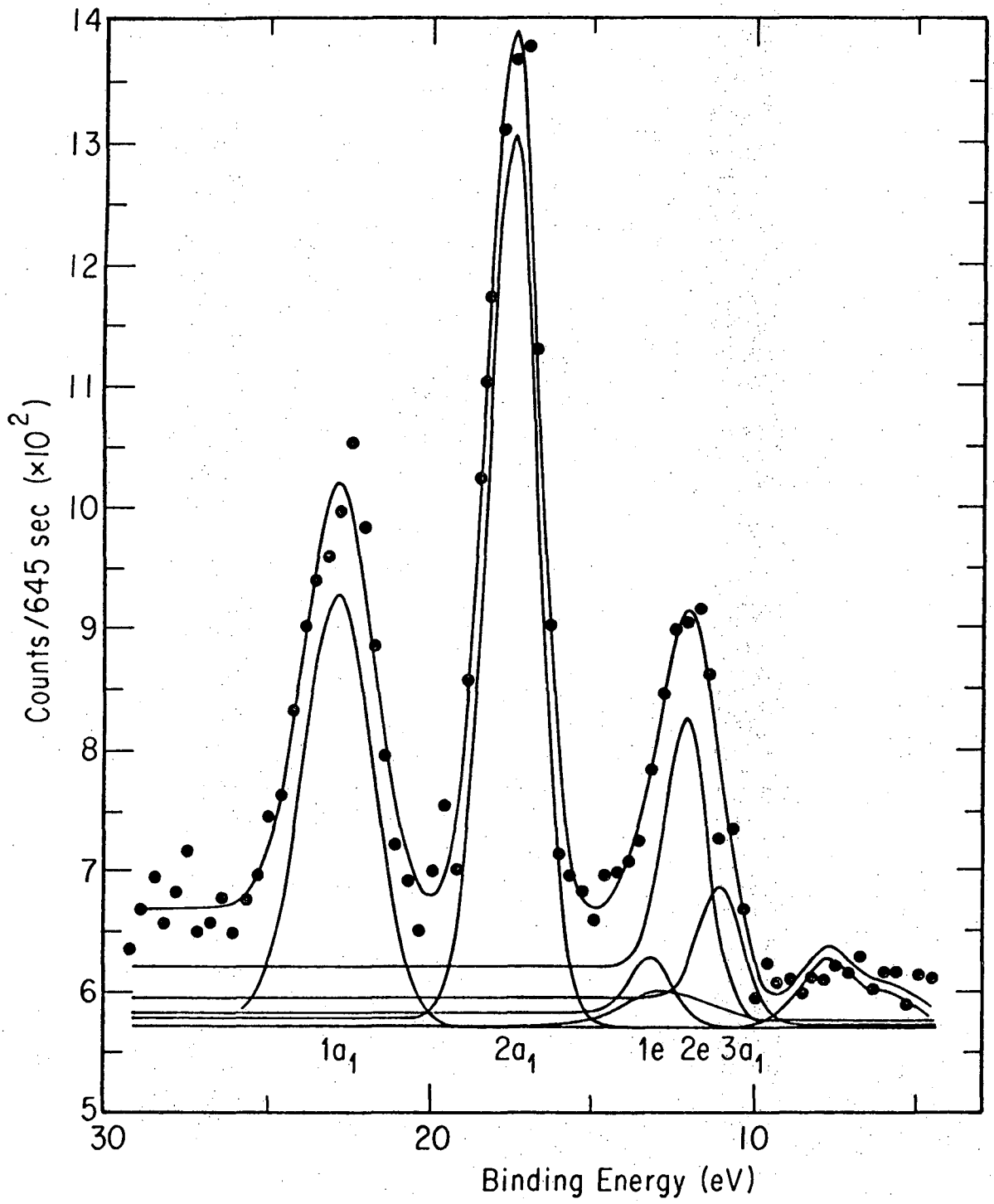

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Fig. 2

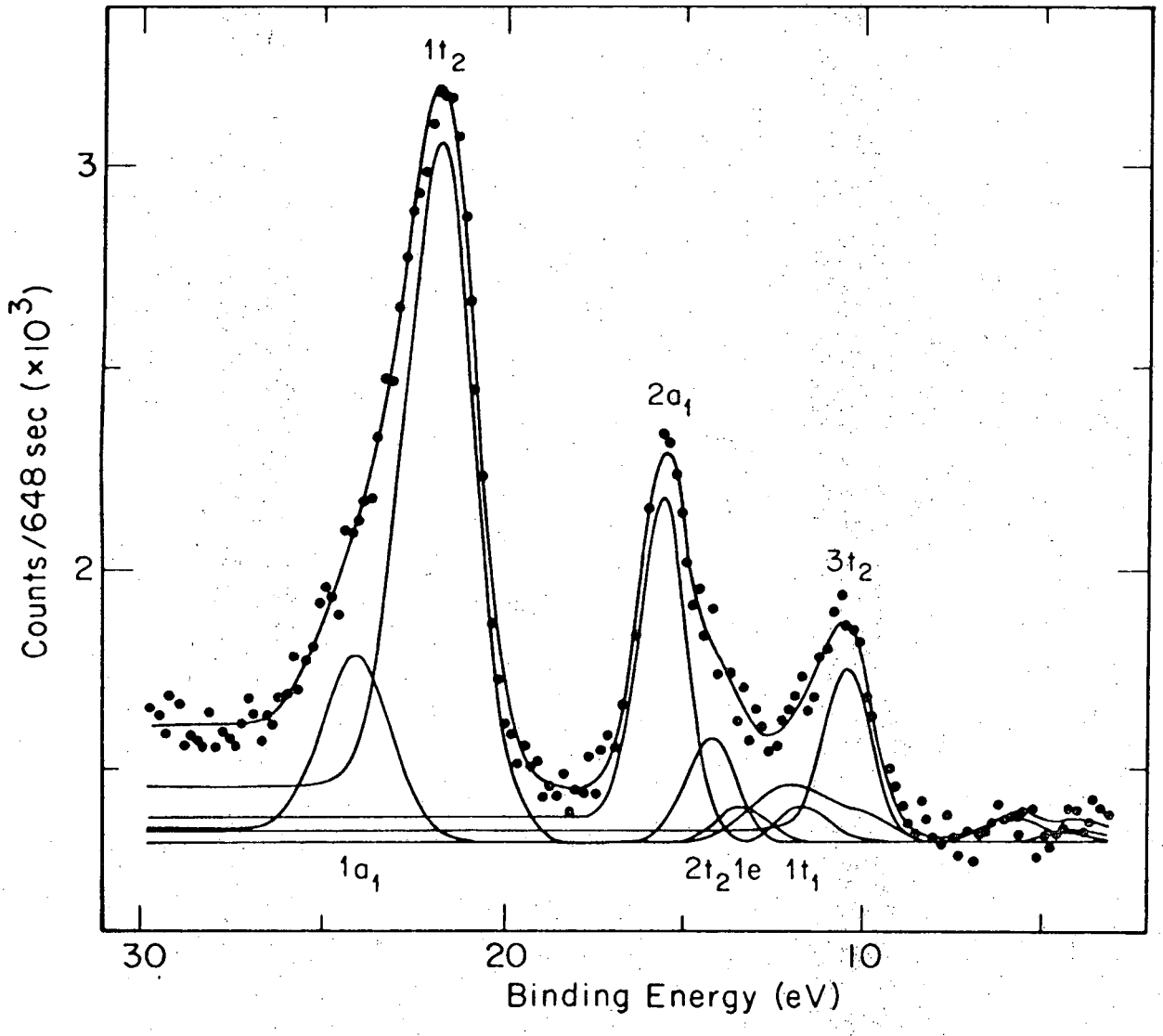

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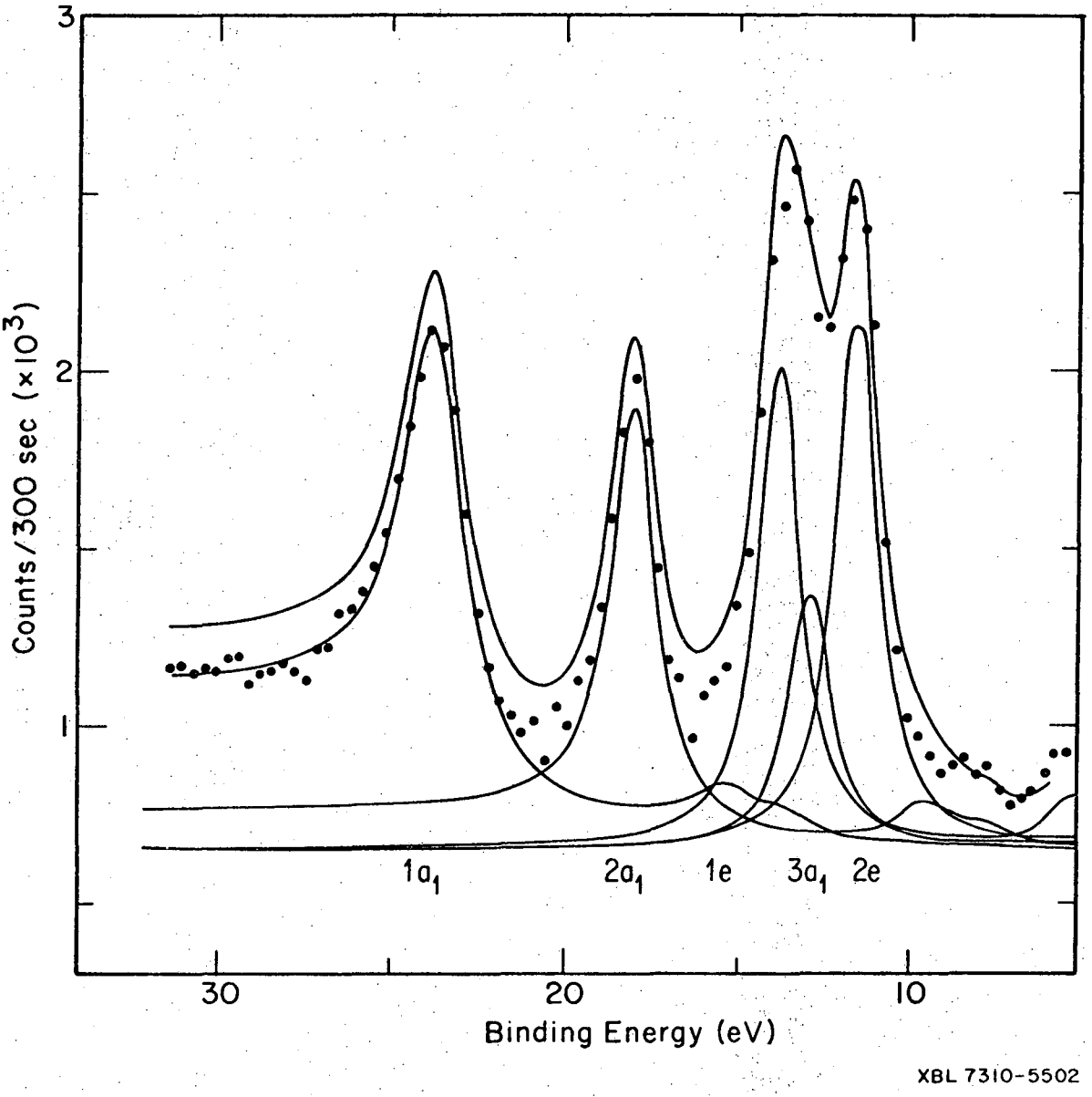
Fig. 3


3
2
1
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1e
3a₁
2e
30
20
10
Binding Energy (eV)
XBL 7310-5502

Fig. 4

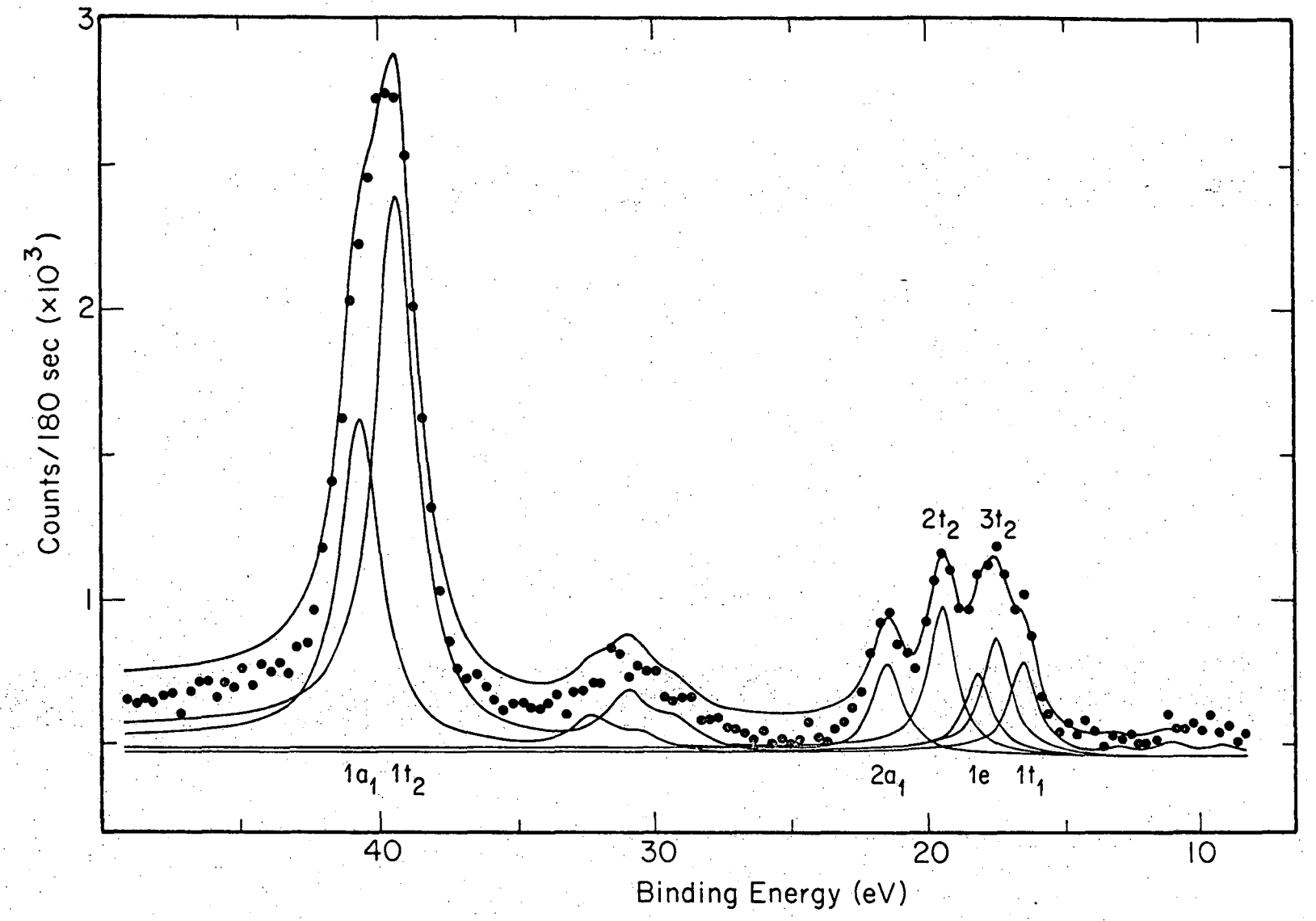

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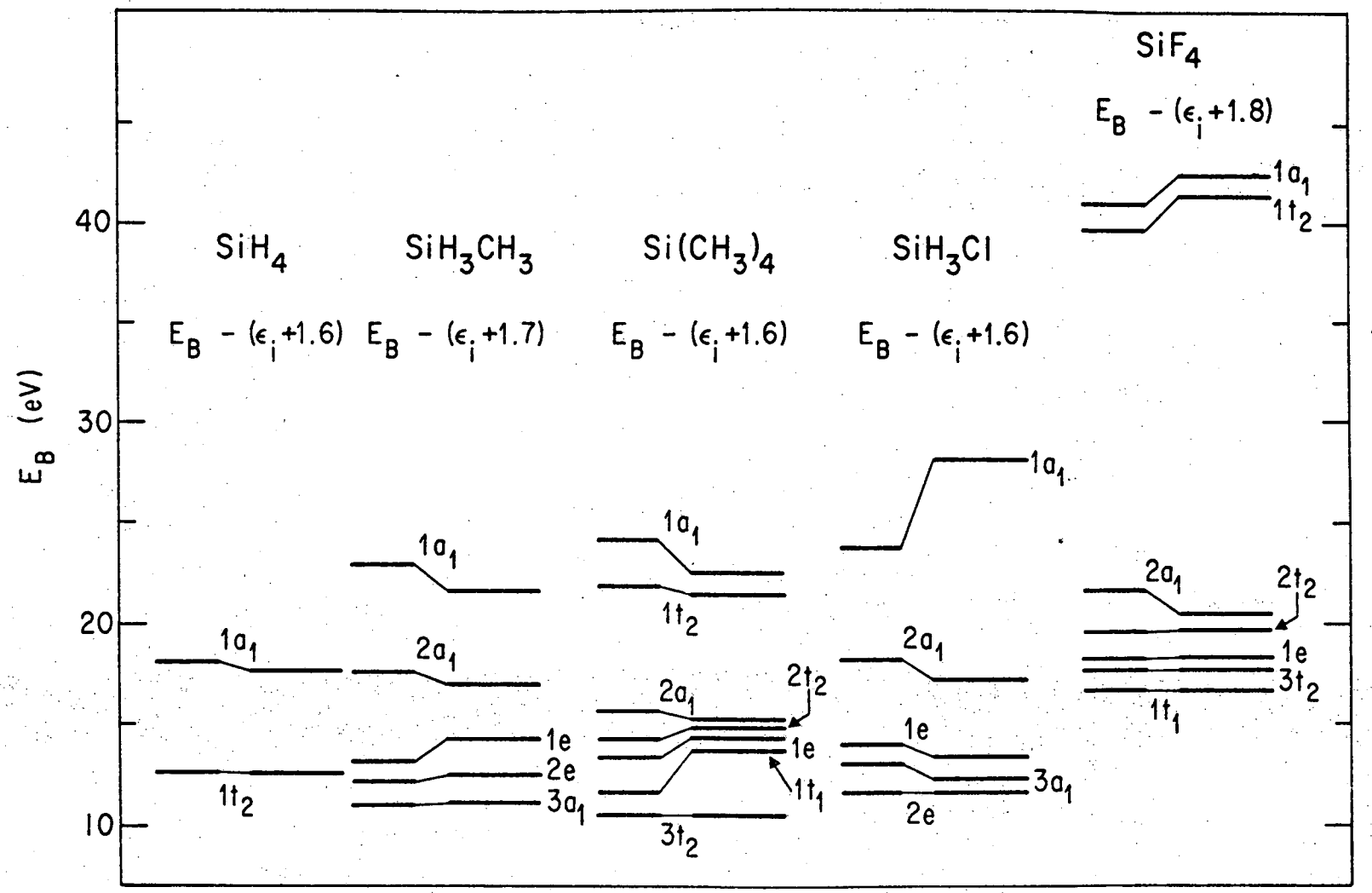
Fig. 5



XBL 7310-5562

Fig. 6

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