Title

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Authors

Kramer, L.N.
Klein, M.P.

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L. N. Kramer and M. P. Klein

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Application of Extended Huckel Theory to X-ray Photoelectron Spectroscopy. Correlations Between Electron Binding Energy and Calculated Atomic Charge in Iron And Sulfur Compounds

L. N. Kramer and M. P. Klein

Laboratory of Chemical Biodynamics, Lawrence Radiation Laboratory

University of California, Berkeley California

ABSTRACT

Extended Hückel M.O. calculations are used to help interpret X-ray photoelectron spectra of iron and sulfur in a diverse series of iron and sulfur compounds. Atomic charge, calculated by this semiquantitative method, is correlated with the measured Fe3P and S2P electron binding energies. It is shown that the calculated charge is correlated directly with calculated Fe3P binding energies in a representative series of iron compounds when using the approximations of extended Hückel theory. The measured binding energies of formally charged ionic iron complexes, however, depart from the charge vs. measured binding energy correlations of neutral iron molecules, and this is attributed to lattice effects and to overemphasis of covalency in the calculations. The use of S.C.F. Slater wave functions and the inclusion of d orbitals on sulfur atoms result in improved correlations between charge and measured S2P binding energies for sulfur compounds. The limitations of this method are discussed briefly.

INTRODUCTION

A potentially useful application of photoelectron spectroscopy is the elucidation of the structure and bonding characteristics of active biological systems. A large number of active sites involve transition metals of uncertain moieties. One group of such systems is the important electron transport non-heme iron proteins,[1] in which an iron-sulfur arrangement, acting as an active redox site, is implicated.

In order to help interpret the photoelectron spectra of these iron proteins, we have set up a correlation between the measured Fe3P electron binding energies (B.E.s) and the calculated iron charge in a diverse series of iron compounds. A similar correlation has been established for S2P electron B.E.s in representative sulfur compounds. Because of the large electronic systems involved in transition metal compounds, ab initio M.O.-S.C.F. calculations are extremely difficult, if not impossible, at the present time. In order to obtain at least semiquantitative understanding of photoelectron chemical shifts in these compounds, we have used the extended Hückel M.O. method to calculate the atomic charges used in our correlations for iron and sulfur compounds

Similar correlations have been attempted by other workers. Siegbahn et al.[2] have correlated photoelectron chemical shifts with fractional atomic charges calculated by a modification of Pauling's method in simple sulfur, nitrogen, and carbon compounds. For the compounds investigated, their correlations are generally good and can be used as a rough estimate of some bonding characteristics such as resonance structures and ligand

environment, Siegbahn's group has also performed ab initio M.O.-S.C.F. calculations on simple sulfur and carbon compounds, resulting in good agreement between calculated and measured B.E. Hendrickson et al.[3,4] have had varying degrees of success in correlating photoelectron chemical shifts with charge calculated by means of the CNDO and extended Hückel methods in nitrogen and phosphorous compounds. The success of these semiquantitative M.O. methods depends on the validity of the approximations made. Fadley et al.[5] have related measured B.E. with calculations of free ion states modified by Madelung and relaxation corrections for fluorine, chlorine, bromine, iodine, and europium. Ground state S.C.F.-M.O. calculations (using Koopman's theorem) were performed by Bash and Snyder on simple molecules containing carbon, nitrogen, fluorine and oxygen. The calculated K-shell binding energies, when plotted against Mulliken net charge, show an approximate linear relationship.[6]

Blyholder and Coulson[7] have shown that the Hoffmann extended Hückel formalism can reasonably approximate the more accurate Hartree-Fock S.C.F. Hamiltonian matrix elements within the limits of certain assumptions. Although the approximations involved do not result in high accuracy, extended Hückel calculations should give satisfactory results for charge and one electron energy calculations. It is desired that the self-consistency of these calculations is such that by using the same empirical parameters for a series of molecules, one can obtain a suitable correlation plot of either calculated charge or electron binding energy. The correlation could then be used to interpret photoelectron spectra with respect to the electronic and structural environment of a particular molecule.

The primary assumptions in making such correlations are: (1) experimental work function variations among solid samples are small; (2) electronic relaxation effects are relatively constant; (3) lattice effects are compensated within the extended Hückel formalism or its modifications; and (4) the extended Hückel approximations are reasonably valid.

METHOD OF CALCULATION

Both charge and binding energy were calculated using an extended Hückel molecular orbital method formulated by Hoffmann,[8,9] with modifications[10] to the Coulomb integrals and Slater exponents such that iteration to charge self-consistency could be obtained. Coulomb integrals were approximated by Valence Orbital Ionization Potentials[11] (choosing an electronic configuration of d^6sp for the iron atom). Off-diagonal elements of the secular determinant were approximated by Cusach's[12] formula

$$H_{ij} = \frac{S_{ij}(H_{ii} + H_{jj})\ (2 - |S_{ij}|\ )}{2}$$

where H and S represent the appropriate Coulomb and overlap integrals, respectively. Slater-type orbitals were used for the minimum basis set of wave functions. Slater's rules[13] were used for wave function parameters in both the iron and sulfur calculations. Self-consistent field Slater-type functions of Clementi and Raimondi[14] were also used for the sulfur calculations, including d

orbitals on the sulfur. Somewhat arbitrary values (though roughly consistent with previous work[10,15]) of 1.00 for the Slater exponent and 1.00 eV for the ionization potential of the d electrons of sulfur were used in the latter calculations. Charge values, made self-consistent to 0.05 charge units through iteration, were obtained by Mulliken's method of population analysis.[16] Coordinates, bond distances, and bond angles were obtained from appropriate literature sources, and, in some cases, Quantum Chemistry Program PROXYZ[17] was used to obtain suitable coordinates. Large molecular structures such as the iron phthalocyanine and dithiocarbamates were approximated by replacing peripheral carbon substituents with hydrogen atoms.

EXPERIMENTAL

Spectra were produced and analyzed in the Berkeley iron-free electron spectrometer.[18] The widths at half maximum of the Fe3P and S2P photoelectron lines are about 2.6 eV and 2.4 eV, respectively. Photoelectron line positions were reproducible to about 0.2 eV. Figure 1 shows representative Fe3P and S2P photoelectron lines.

All measured electron binding energies were referenced to the B.E. of the C1S electrons of the spectrometer diffusion pump oil, deposited on the surface of our samples. The work function of the spectrometer was taken as 4 eV, and the C1S electron B.E. of the oil was defined as 284.0 eV.

Published synthetic procedures were followed in the preparation of the following compounds: iron(N,N-diethyldithiocarbamate), $Fe(S_2CNC_2H_6C_2H_6)_3$;[19] K_2FeO_4;[20] tetra-n-butylammonium-bis(toluene-3,4-dithiolate)iron; $Fe(S_2C_6H_3CH_3)_2^- \cdot N(n\text{-}C_4H_9)_4^+$;[21] $KFeS_2$;[22] $Fe^{+3}Cl$ phthalocyanine.[23]

Monobrombis (N,N-dialkyldithiocarbamato)iron, $FeBr(S_2CNC_2H_6C_4H_4)_2$ was obtained from Dr. H. H. Wickman. The ferrocenium picrate, $[Fe(C_5H_5)^+_2 \cdot (NO_2)_3C_6H_2O)^-]$ was obtained from Dr. D. N. Hendrickson Ferrichrome A was obtained from Professor J. B. Neilands. All other compounds were obtained from commercial sources.

Computations were carried out using the CDC 6600 computer of the Lawrence Radiation Laboratory in Berkeley. Calculations were performed on only those compounds for which both structure data and photoelectron spectra could be applied unambiguously.

RESULTS AND DISCUSSION

Table I lists the calculated Fe3P electron binding energies and the corresponding calculated iron charges for representative iron compounds. The Fe3P B.E.s were calculated by including the Fe3P electrons in the molecular orbital calculation and using the resulting one electron energies of the three lowest molecular orbitals as the Fe3P binding energies. Figure 2 shows the corresponding plot of charge vs. electron B.E. This plot shows a direct correlation between calculated electron binding energy and calculated charge for a representative sampling of iron compounds. From this observation it seems reasonable to expect similar results if attempts are made to correlate measured electron B.E.s with either calculated charge or calculated electron B.E.s resulting from this extended Huckel method of calculation. Since it is much easier to calculate charge (fewer orbitals being necessary in the calculations), especially for large molecules, we have concentrated on establishing

correlations with calculated charge rather than calculated B.E.

Table II lists the measured Fe3P electron B.E.s and calculated charges for those compounds under investigation; figure 3 shows the corresponding plot of measured B.E. vs. calculated charge. The line drawn through the points is a least squares fit to the data from neutral molecules. From this plot, it is apparent that the data point positions of formally charged ionic complexes depart from those of neutral molecules in a relatively consistent manner.

There are two important factors which contribute to this variance with neutral molecule data. One factor is the lattice potential effect and the other is the overemphasis of covalency in ionic molecules when using the extended Hückel method. The quantitative treatment of these factors is not straightforward because of the lack of adequate, non-classical lattice potential calculations, and because of the breakdown of the extended Hückel approximations for highly ionic complexes. The effect of the periodic lattice potential on the electron B.E.s will depend primarily upon core-electron attractions and electron-electron repulsions. These will have opposing effects; core-electron attractions will increase electron B.E., while electron-electron repulsion will decrease electron B.E. If lattice potential effects are assumed to dominate the factors contributing to variance from neutral molecule data, then the data of figure 3 suggests that core-electron attractions have the greater magnitude.

We have empirically corrected the electron B.E.s of the formally charged complexes through the use of the following relationship

$$\Delta E = CQ^2 I$$

where ΔE is the electron B.E. correction, C is a proportionality constant (1.5, in this case), Q^2 is the square of the iron atomic charge, and I is the ionicity of the neutral metal-ligand bond as defined by Pauling's[24] relationship, $I=1-\exp[-0.25(X_A-X_B)^2]$, where X_A and X_B are the electonegativities of the metal and ligand. The CQ^2 term is empirically derived from the data and represents the magnitude of the effects from the lattice potential and the overemphasis of covalency. The ionicity parameter, I, reflects the attenuation of the effects in question due to the covalency of the molecular bonding.

The modified Fe3P electron B.E.s are listed in Table II, and the corresponding plot of modified B.E.s vs. calculated charges is shown in figure 4. Only compounds 1 through 6 and compounds 9 and 15 have been corrected for B.E. The bond ionicities of these compounds are taken as 0.6, 0.45, 0.45, 0.45, 0.1, 0.1, 0.1, and 0.1 respectively. (Although the bond ionicities of the hexahydrates should actually be larger than indicated, the value of 0.45 is used to maintain consistency with the correction formula presented above.)

Table III lists the measured S2P electron B.E.s and the calculated charges determined with the use of simple Slater wave functions, and also, the charges calculated with the use of S.C.F. Slater wave functions. Sulfur d orbitals were included when using the S.C.F. wave functions, and in all cases, only a minimal basis set was used. Figures 5 and 6 show the corresponding plot of measured S2P B.E.s vs calculated sulfur charge.

S.C.F. wave function parameters were not used for the iron series calculations because of the difficulties in obtaining charge self-consistency using d orbitals on the sulfur in iron-sulfur complexes. Furthermore, the few simple iron compounds tested using S.C.F. wave function parameters showed no improvement in the charge correlation with electron B.E.

Considering the assumptions made in carrying out these calculations, the resulting atomic charges show a relatively good correlation with the corresponding measured B.E.s provided one accepts the argument for B.E. correction in formally charged ionic complexes. The success of these correlations supports the suggestion made previously[25] that chemical shifts in the core electron B.E.s of an iron atom (or, more generally, any atom) are related to changes in its total electronic environment rather than simply to its formal oxidation state. Ideally then, one should be able to distinguish between electronic environments by measuring the electronic B.E. and then using a charge vs. B.E. correlation to help elucidate the electronic bonding features. In practice, however, there may be complexes which are not in such good agreement with this correlation, but at least approximate agreement can be expected.

CONCLUSIONS

In the introduction it was pointed out that several assumptions must be made in any attempt to correlate atomic charge with measured B.E. Furthermore, it should be noted that if unrestricted *ab initio* calculations (including relaxation effects) were possible for the compounds we have investigated, there would be no reason to expect a *simple* charge vs. B.E. correlation. The observation that our calculations show reasonable correlations between atomic charge and measured B.E. indicates that the assumptions are relatively good. However, the correlations are admittedly somewhat artificial since the simple extended Hückel calculations are insensitive to some important contributions to electron energy, which include relativistic, electron correlation, and relaxation effects. Nevertheless, until *ab initio* calculations can be applied easily to large electronic systems, semiquantitative methods, such as used here, may be very useful aids in understanding structural and bonding phenomena.

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Table I. Calculated Fe3P electron binding energies and the corresponding iron charges for representative iron compounds

No.	Molecule	Calc. B.E. (eV)	Calc. charge
1	$FeF_6^{\equiv}$ (K_3KeF_6)	59.6	+1.81
2	$FeO_4^{=}$ (K_2FeO_4)	59.7	+1.79
3	Ferrichrome A	59.06	+1.53
4	$Fe(CO)_5$	58.3	+1.02
5	$Fe(C_5H_5)_2$	58.1	+1.0
6	$FeBr(S_2CNC_2H_6C_4H_4)_2$	57.7	+0.82
7	FeS_2	56.9	+0.45
8	Fe	56.0 (defined)	0 (defined)

Table II

Measured Fe3P electron binding energies, calculated charges, and binding energies modified for lattice and ionicity effects. Binding energies are reproducible to about 0.2 eV and charges are self-consistent to 0.05 charge units

No.	Molecule	Measured Fe3P B.E. (eV)	Calc. iron charge	Modified Fe3P B.E. (eV)
1	$FeF_6^{=}$ (K_3FeF_6)	57.7	+1.8	54.9
2	$FeO_4^{=}$ (K_2FeO_4)	57.7	+1.79	55.5
3	$Fe(H_2O)_6^{+3}$ ($Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 24H_2O$)	56.6	+1.51	55.1
4	$Fe(H_2O)_6^{+2}$ ($FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$)	54.2	+0.86	53.7
5	$Fe(CN)_6^{-3}$ ($K_3Fe(CN)_6$)	55.0	+1.24	54.8
6	$Fe(CN)_6^{-4}$ ($K_4Fe(CN)_6$)	54.0	+1.03	53.8
7	Fe (metal)	52.4	0 (defined)	—
8	$Fe(C_5H_5)_2$	53.7	+1.0	—

Table II (Cont.)

No.	Molecule	Measured Fe3P B.E. (eV)	Calc. iron charge	Modified Fe3P B.E. (eV)
9	$Fe(C_5H_5)_2^+$ $[Fe(C_5H_5)_2^+ \cdot (NO_2)_3C_6H_2O^-]$	54.9	+1.36	54.7
10	$Fe(CO)_5$	54.0	+1.02	—
11	$Fe_2(CO)_9$	54.6	+1.3	—
12	FeS_2	53.0	+0.45	—
13	$Fe(S_2CNC_2H_6C_2H_6)_3$	53.5	+0.95	—
14	$FeBr(S_2CNC_2H_6C_4H_4)_2$	54.0	+0.82	—
15	$Fe(S_2C_6H_3CH_3)^-$ $[Fe(S_2C_6H_3CH_3)_2^- \cdot N(n\text{-}C_4H_9)_4^+]$	53.2	+0.29	53.1
16	Ferrichrome A	54.9	+1.53	—
17	Hemin Cl	54.2	+1.04	—
18	$Fe^{+3}Cl$ Phthalocyanine	54.4	+1.46	—

Table III

Measured S2P electron binding energies and charges calculated through the use of both simple Slater wave functions and S.C.F. Slater wave functions including sulfur d orbitals. Binding energies marked with an asterisk were taken from Ref. 2, suitably corrected by a single additive constant to achieve agreement between spectrometers. Binding energies are reproducible to about 0.2 eV and charges are self-consistent to 0.05 charge units

No.	Molecule	Measured S2P B.E. (eV)	Calc. sulfur charge-Slater	Calc. sulfur charge-SCF
1	$SO_4^=$	167.8	+1.86	+1.69
2	$SO_3^=$	166.4	+1.40	+1.12
3	CH_3SOCH_3	165.5*	+0.70	+1.0
4	CH_3SSCH_3	163.3*	-0.13	+0.02
5	CH_3SH	162.6*	+0.09	+0.26
6	FeS_2	161.5	-0.22	-0.15
7	FeS	160.7	-0.43	-0.5
8	$Fe(S_2CNETET)_3$	161.5	-0.3	---
9	$FeBr(S_2CNETET)_2$	161.4	-0.3	---
10	$Fe(S_2C_6H_3CH_3)_2$	161.4	-0.43	---
11	$KFeS_2$	161.1	-0.46	---

FIGURE CAPTIONS

Fig. 1. X-ray photoelectron spectral lines of Fe3P and S2P electrons excited by AlKα radiation. The full width at half maximum is 2.6 eV for iron and 2.4 eV for S.

Fig. 2. Calculated binding energies of Fe3P electrons vs. calculated charge. All values are referred to neutral Fe whose 3P binding energy is arbitrarily set equal to 56.0 eV. The numbered points refer to the compounds listed in Table I.

Fig. 3. Measured Fe3P electron binding energies vs. calculated charge for a diverse series of iron compounds. The numbered points refer to compounds listed in Table II.

Fig. 4. Fe3P electron binding energies (modified for lattice and ionicity effects) vs. calculated charge. The numbered points refer to compounds listed in Table III.

Fig. 5. Measured S2P electron binding energies vs. calculated charge using simple Slater wavefunctions. The numbered points refer to the compounds listed in Table III.

Fig. 6. Measured S2P electron binding energies vs. calculated charge using S.C.F. Slater wave functions and including sulfur d orbitals. The numbered points refer to the compounds listed in Table III.

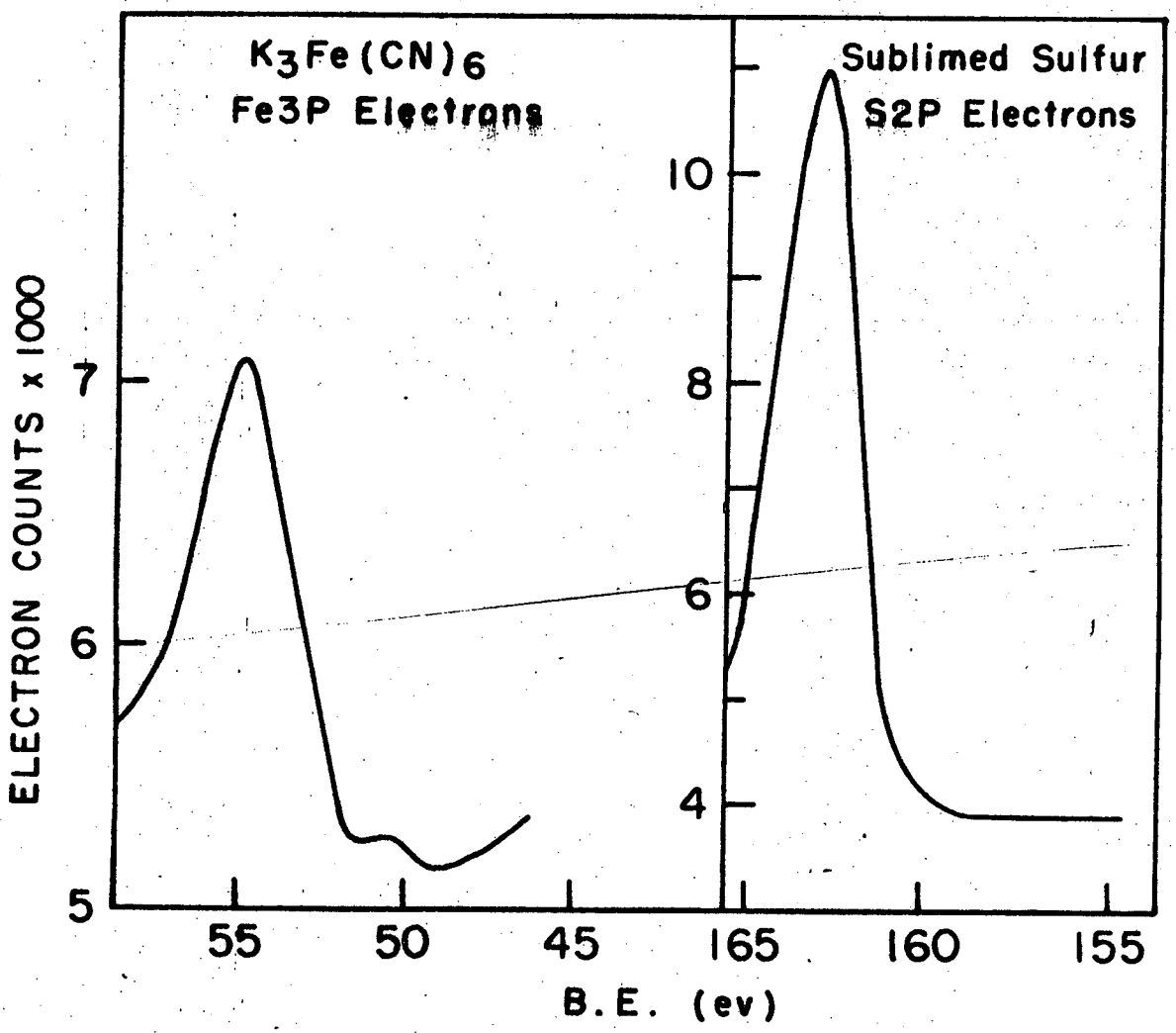
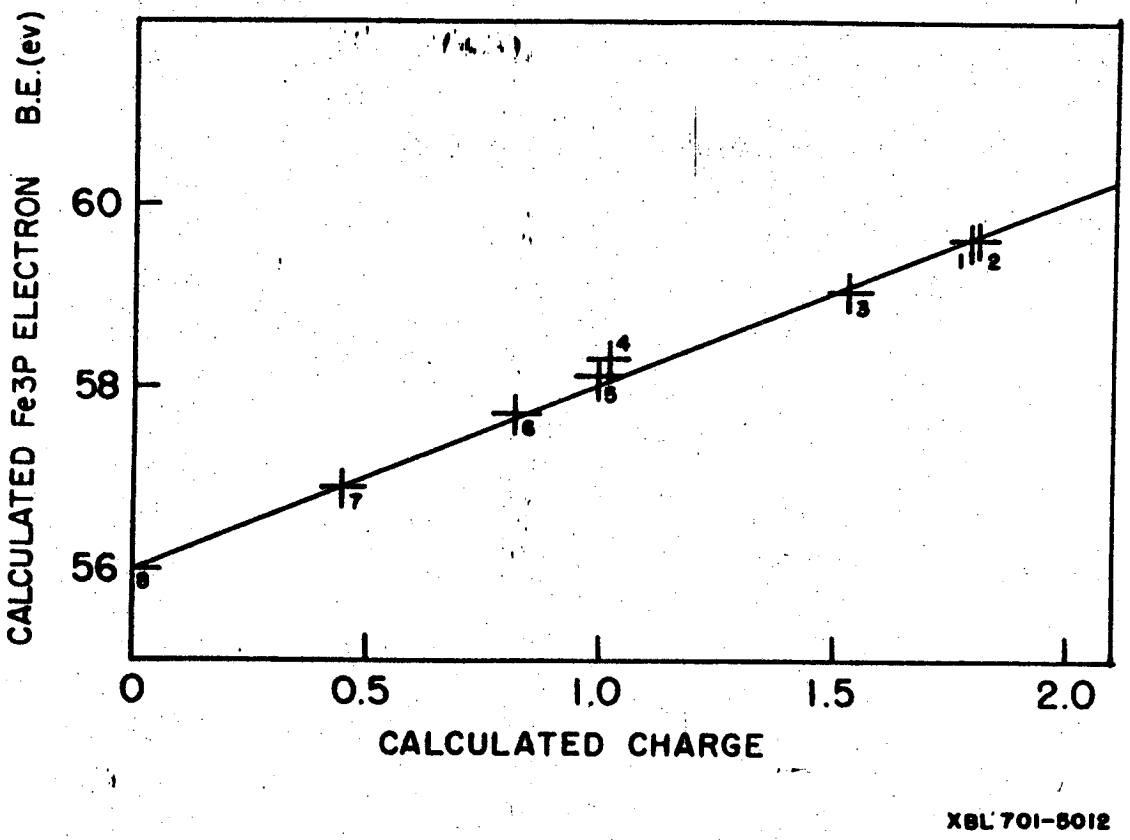

$K_3Fe(CN)_6$
Fe3P Electrons
Sublimed Sulfur
S2P Electrons
ELECTRON COUNTS x 1000
7
6
5
10
8
6
4
55
50
45
165
160
155
B.E. (ev)
XBL 701-5013

Fig. 1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56
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1.5
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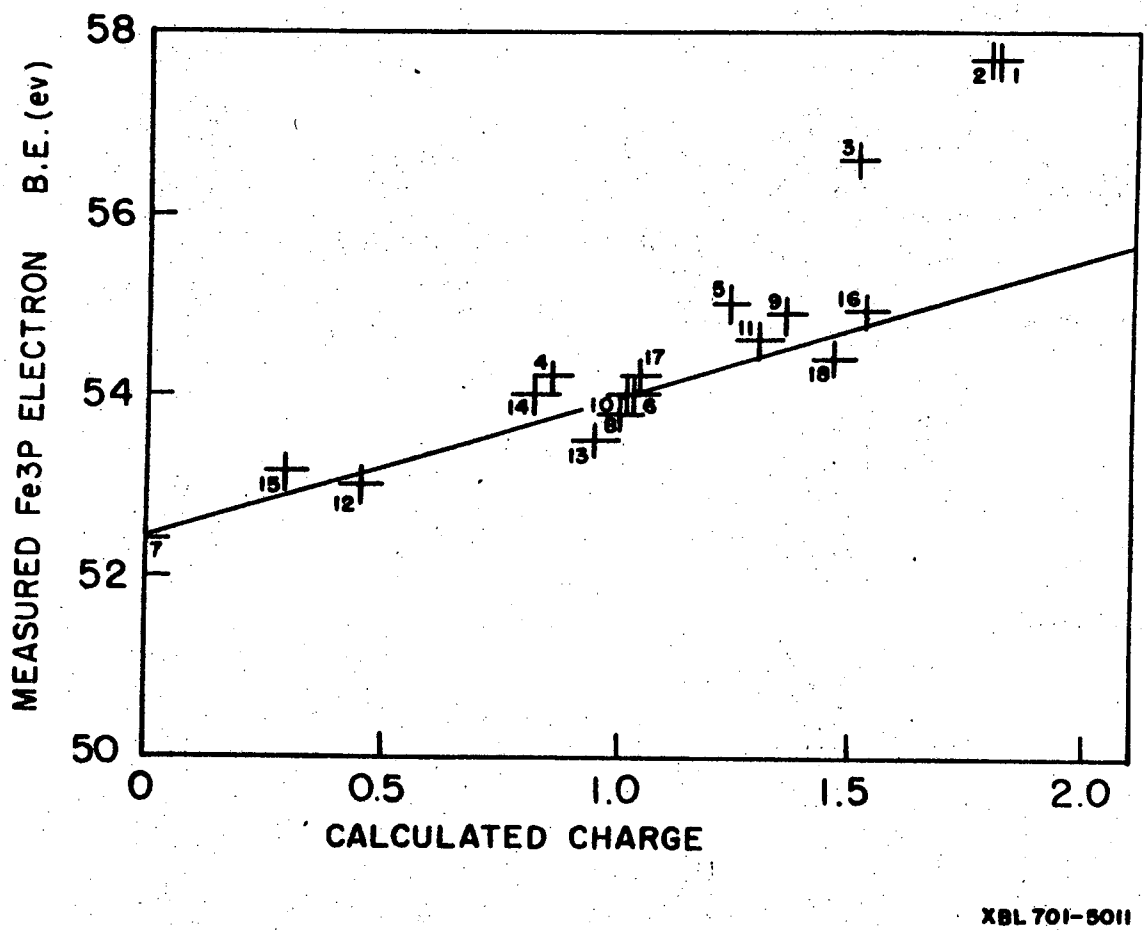
CALCULATED CHARGE
XBL 701-5012

Fig. 2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56
54
52
50
0
0.5
1.0
1.5
2.0
CALCULATED CHARGE
1
2
3
4
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7
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11
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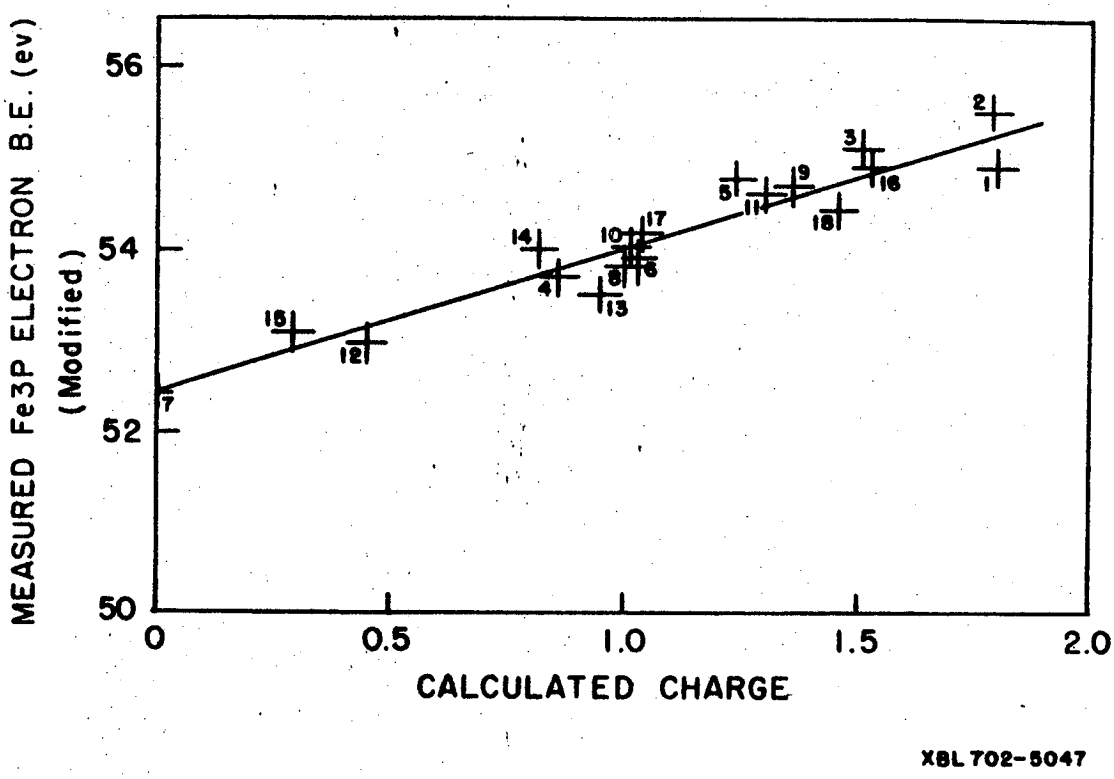
17
18
XBL 701-5011

Fig. 3


MEASURED Fe3P ELECTRON B.E. (ev)
(Modified)
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54
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50
0
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1.0
1.5
2.0
CALCULATED CHARGE
1
2
3
4
5
6
7
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9
10
11
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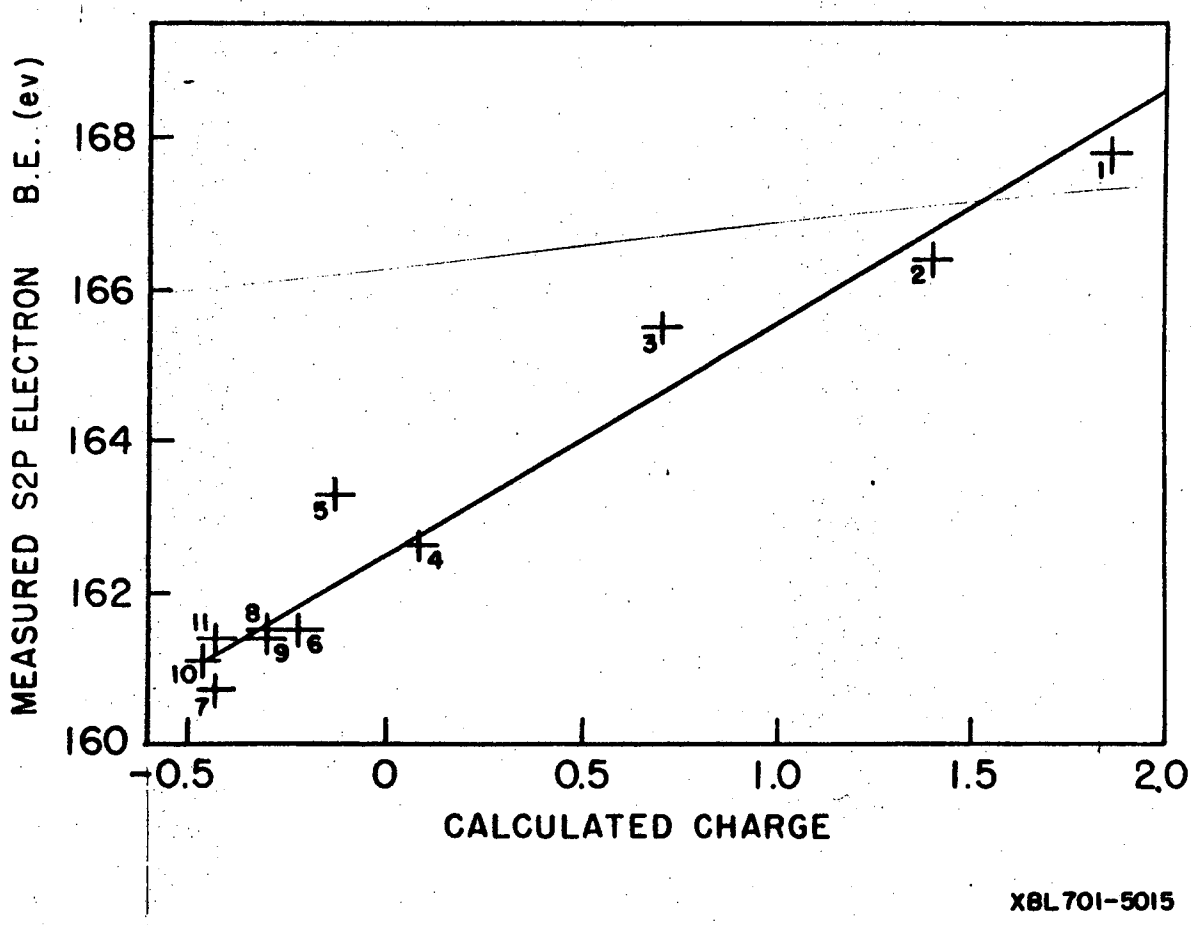
16
17
18
XBL 702-5047

Fig. 4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1.5
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CALCULATED CHARGE
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10
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XBL701-5015

Fig. 5

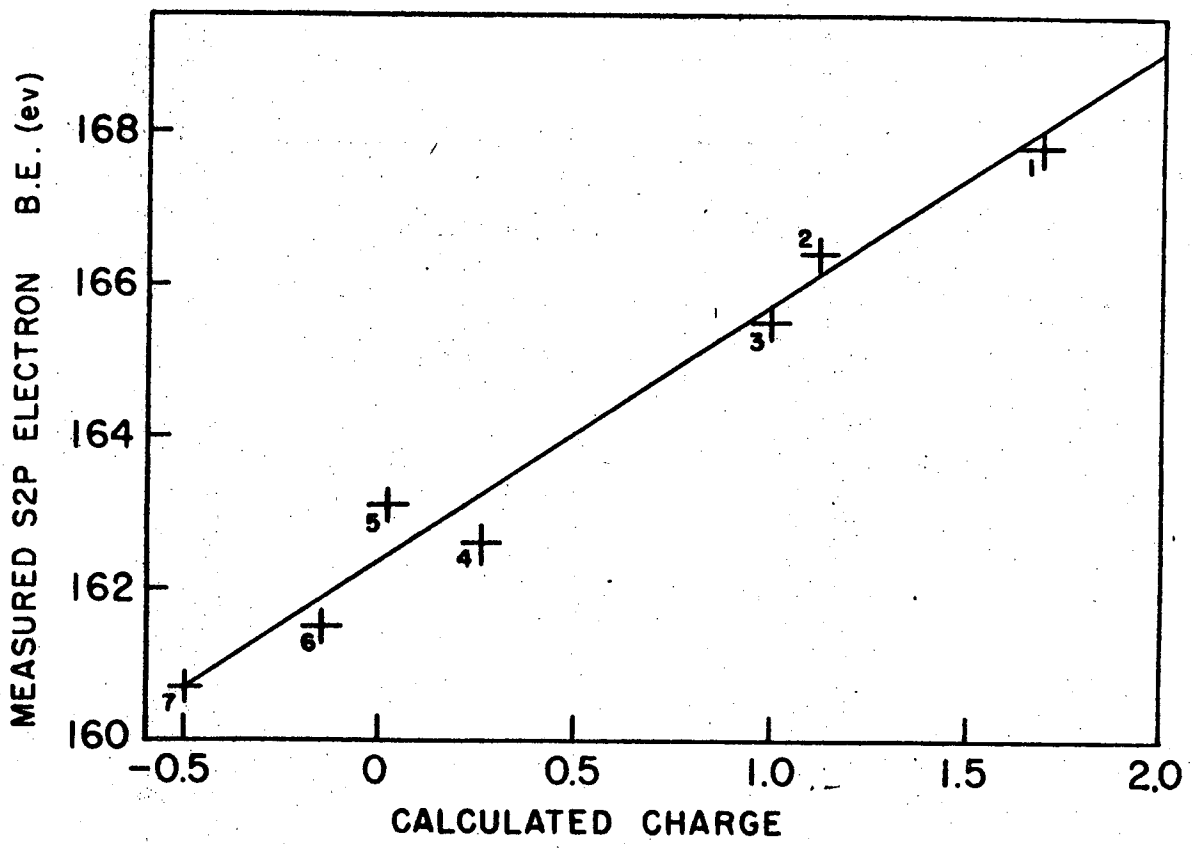

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Fig. 6

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