

Lawrence Berkeley National Laboratory

Recent Work

Title

CHEMICAL BONDING INFORMATION FROM PHOTO-ELECTRON SPECTROSCOPY

Permalink

<https://escholarship.org/uc/item/7bn2b045>

Authors

Fadley, C.S.

Hagstrom, S.B.M.

Hollander, J.M.

et al.

Publication Date

1967-05-01

cy. 2

University of California

Ernest O. Lawrence Radiation Laboratory

CHEMICAL BONDING INFORMATION FROM PHOTOELECTRON SPECTROSCOPY

C. S. Fadley, S. B. M. Hagström, J. M. Hollander,
M. P. Klein, and D. A. Shirley

May 1967

RECEIVED
LAWRENCE
RADIATION LABORATORY

JUL 26 1967

LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 5545

UCRL-17426 Rev.

cy. 2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to Science

UCRL-17426-Rev.
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

CHEMICAL BONDING INFORMATION FROM PHOTOELECTRON SPECTROSCOPY

C. S. Fadley, S. B. M. Hagström, J. M. Hollander, M. P. Klein, and
D. A. Shirley

May 1967

CHEMICAL BONDING INFORMATION FROM PHOTOELECTRON SPECTROSCOPY

Techniques of general applicability are demonstrated on iodine and europium compounds.

C. S. Fadley, S. B. M. Hagström, J. M. Hollander, M. P. Klein, and
D. A. Shirley

Author note:

Dr. Hagström is presently with the Physics Department at the Chalmers University of Technology, Gothenburg, Sweden. The other authors are with the Nuclear Chemistry Division and the Chemical Biodynamics Laboratory, Lawrence Radiation Laboratory, University of California, Berkeley, California.

Introduction

Recently a new spectroscopic method, developed by K. Siegbahn and collaborators in Uppsala (1), has found application in elementary chemical analysis (2), and in studies of chemical bonding (3-6). The principle of the method is to deduce the binding energies of the inner core electrons of an atom from very accurate measurements of x-ray produced photoelectron spectra. Its utility as a tool for chemical bonding studies arises from the observation that the electron binding energies are sensitive to the chemical environment of a given atom; such chemically-induced shifts in the core-electron binding energies have been measured in carbon (3), nitrogen (4), oxygen (3), sulfur (5), and chlorine (6).

We report here the results of a study on two heavier elements, iodine and europium (7), in which the core-electron binding energies were measured as a function of the oxidation number of the atom of interest. In iodine, we observed a shift in the core level energies of 0.8 eV per unit change in oxidation number; in europium the corresponding shift was 9.6 eV.

We propose two theoretical models in terms of which our observed core-level shifts can be understood. The first uses a charged-shell approximation for the molecular orbitals, while the second makes use of an energy cycle to divide the binding energy into a free-ion term and a lattice interaction (Madelung) term.

We also discuss several other promising applications of the photoelectron spectroscopic technique.

Experimental Procedure

The experimental technique involves expelling an electron from a level, i , of an atom A with x-radiation greater in energy than the binding energy. Neglecting contact potential effects, the energy conservation equation is

$$h\nu = E_p(A, i, X) + E_{kin} \quad (1)$$

where $h\nu$ is the x-ray energy, $E_p(A, i, X)$ is the binding energy of the i -th level of atom A in compound X , and E_{kin} is the photoelectron kinetic energy. Since x-ray energies have been determined previously to high accuracy, only the kinetic energy need be measured to obtain a binding energy. For this purpose a high-resolution magnetic spectrometer was used (8). The energy resolution of this spectrometer was adjusted to 0.06% full width at half maximum, thereby yielding instrumental line widths of 0.6 eV to 4.8 eV over the kinetic energy range of interest (1 to 8 eV). As the natural line widths are also a few eV, it is easily possible to detect shifts in binding energy of the order of one eV with such a spectrometer.

The apparatus is shown schematically in Figure 1. Radiation from the x-ray tube is filtered slightly with aluminum foil and then impinges upon a flat rectangular (10 mm \times 13 mm) powdered sample of the compound under study. Photoelectrons emitted from the sample pass through a defining slit into the spectrometer. For a given current in the spectrometer coils, electrons of a narrow energy range are brought to a focus at the entrance to the Geiger counter. The current is scanned in a stepwise fashion over the region of interest and the resulting pulses from the Geiger counter are stored in a multiscalar (multichannel analyzer). Multiple scans were made in order to average out

References and Notes

1. S. Hagström, C. Nordling, and K. Siegbahn, Table of Electron Binding Energies in Alpha-, Beta-, and Gamma-Ray Spectroscopy, K. Siegbahn, Ed. (North Holland Publishing Co., Amsterdam, 1965).
2. C. Nordling, S. Hagström, and K. Siegbahn, *Zeit. Phys.* 178, 433 (1964).
3. G. Axelson et. al., *Nature* 213, No. 5071, 70 (1967).
4. R. Nordberg et. al., to be published.
5. S. Hagström, C. Nordling, K. Siegbahn, *Z. Physik* 178, 439 (1964).
6. A. Fahlman, R. Carlsson, and K. Siegbahn, *Arkiv Kemi* 25, 301 (1966).
7. C. S. Fadley, S. B. M. Hagström, M. P. Klein, and D. A. Shirley, University of California, Lawrence Radiation Laboratory Report UCRL-17005 (1967). To be submitted to *J. Chem. Phys.*
8. K. Siegbahn, C. Nordling, and J. M. Hollander, University of California, Lawrence Radiation Laboratory Report UCRL-10023 (1962).
9. C. C. J. Roothaan and P. Bagus, Methods in Computational Physics (Academic Press, New York, 1963), Vol. 2.
10. N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals (Clarendon Press, Oxford, 1948), p. 80.
11. D. W. Hafemeister, G. de Pasquali, and H. de Waard, *Phys. Rev.* 135, B1089 (1964).
12. V. Jaccarino, B. F. Matthias, M. Peter, H. Luhl, and J. H. Wernick, *Phys. Rev. Letters* 5, 251 (1960).
13. A. L. Borovik-Romanov and N. M. Kreiss, *Soviet Physics, JETP* 2, 657 (1956).
14. D. I. Arnon, *Science* 149, 1460 (1965); Non-Heme Iron Proteins: Role in Energy Conversion, ed. A. San Pietro (Antioch Press, Yellow Springs, Ohio, 1965).

15. B. H. Schechtman and W. E. Spicer, Bull. Am. Phys. Soc. 11, 899 (1966).
16. The work discussed in this article was done under the auspices of the
U. S. Atomic Energy Commission.

Table 1. Calculated binding energy shifts arising from removal of a 5p electron from various free-ion configurations of iodine. Since the calculations were non-relativistic, levels are not distinguished by the quantum number j , and the notation 2p for example, represents both $2p_{1/2}$ and $2p_{3/2}$.

| | $I^{-1} 5s^2 5p^6$ | $I^0 5s^2 5p^5$ | $I^{+1} 5s^2 5p^4$ | $I^{+2} 5s^2 5p^3$ | $I^{+3} 5s^2 5p^2$ | $I^{+4} 5s^2 5p^1$ |
|-------|------------------------------|---------------------------|---------------------------|---------------------------|---------------------------|--------------------|
| Level | $\Delta E_b(0-[-1])$ (eV) | $\Delta E_b(1-0)$ (eV) | $\Delta E_b(2-1)$ (eV) | $\Delta E_b(3-2)$ (eV) | $\Delta E_b(4-3)$ (eV) | |
| 2s | 8.80 | 9.90 | 10.93 | 12.23 | 13.14 | |
| 2p | 8.79 | 9.87 | 10.93 | 12.19 | 13.16 | |
| 3s | 8.83 | 9.89 | 10.91 | 12.15 | 13.04 | |
| 3p | 8.79 | 9.87 | 10.89 | 12.12 | 13.01 | |
| 3d | 8.78 | 9.87 | 10.89 | 12.15 | 13.06 | |
| 4s | 8.85 | 9.87 | 10.82 | 11.97 | 12.78 | |
| 4p | 8.84 | 9.86 | 10.79 | 11.92 | 12.73 | |
| 4d | 8.84 | 9.85 | 10.78 | 11.92 | 12.72 | |
| 5s | 8.10 | 8.65 | 9.22 | 9.77 | 10.21 | |
| 5p | 8.39 | 9.37 | 10.73 | 9.44 | 9.90 | |

Table 2. Comparison of our results for iodine charge and fractional ionic character in KIO_3 and KIO_4 with those obtained from Mössbauer measurements (reference 11). Those denoted "3/4 Madelung" represent a possible surface correction to our results.

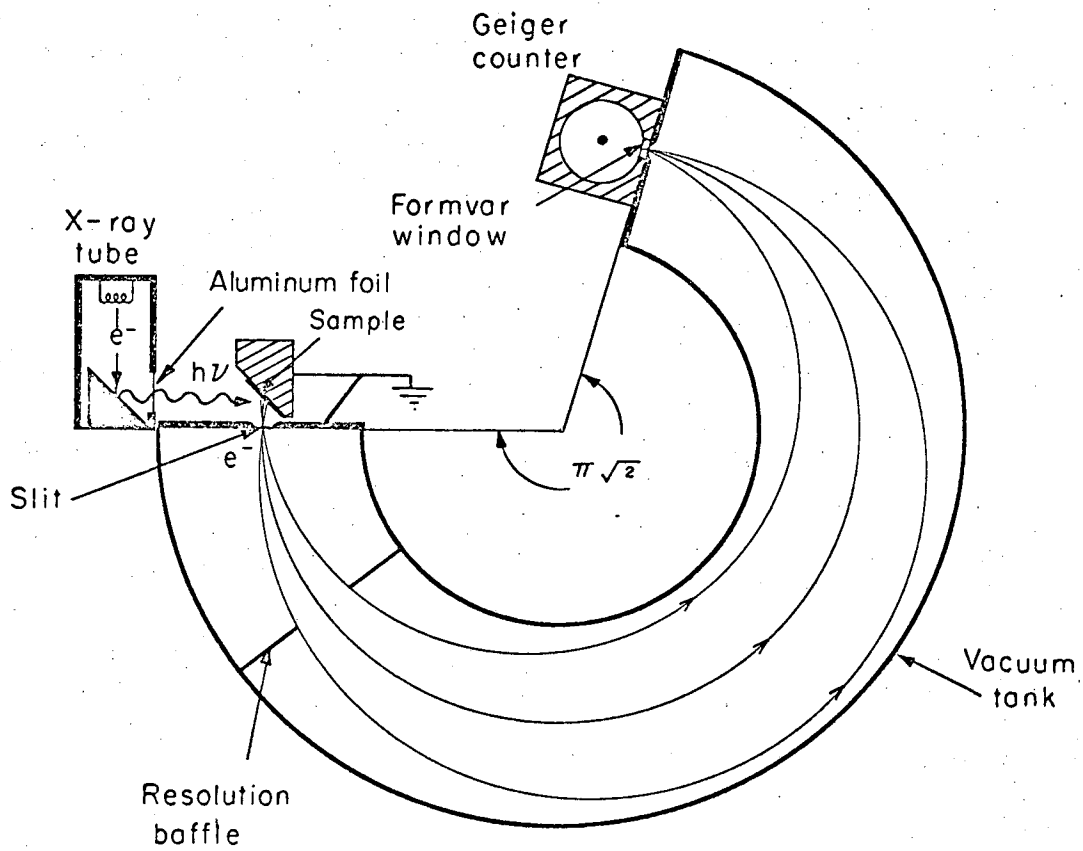
| Compound | I-O bond fractional ionic character | Charge on iodine |
|------------------------------------|--|------------------------|
| <u>Photoelectron spectroscopy:</u> | | |
| Full Madelung- | | |
| KIO_3 | 0.67 | 2.99 |
| KIO_4 | 0.48 | 2.86 |
| 3/4 Madelung- | | |
| KIO_3 | 0.35 | 1.10 |
| KIO_4 | 0.46 | 2.71 |
| ----- | | |
| <u>Mössbauer:</u> | | |
| KIO_3 | 0.31 | 0.83 |
| KIO_4 | 0.31 | 1.44 |

Figure Legends

Fig. 1. Schematic illustration of the experimental apparatus.

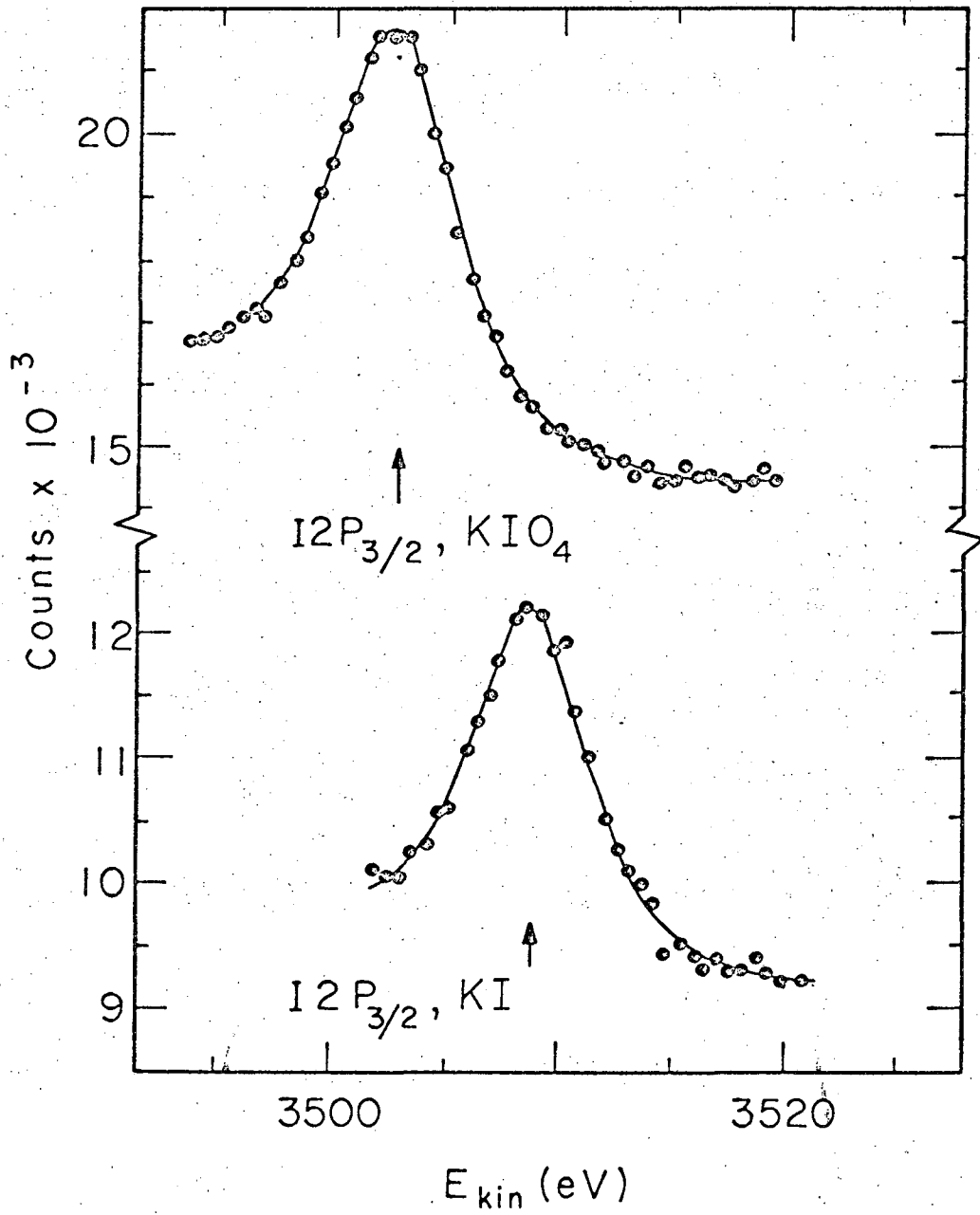
Fig. 2. Photoelectron peaks from KI and KIO_4 .

Fig. 3. Photoelectron peaks from various europium compounds. The oxidation state of the atom is indicated with each peak. The 2 peaks for the +2 state are due to excitation by two different x-ray lines.



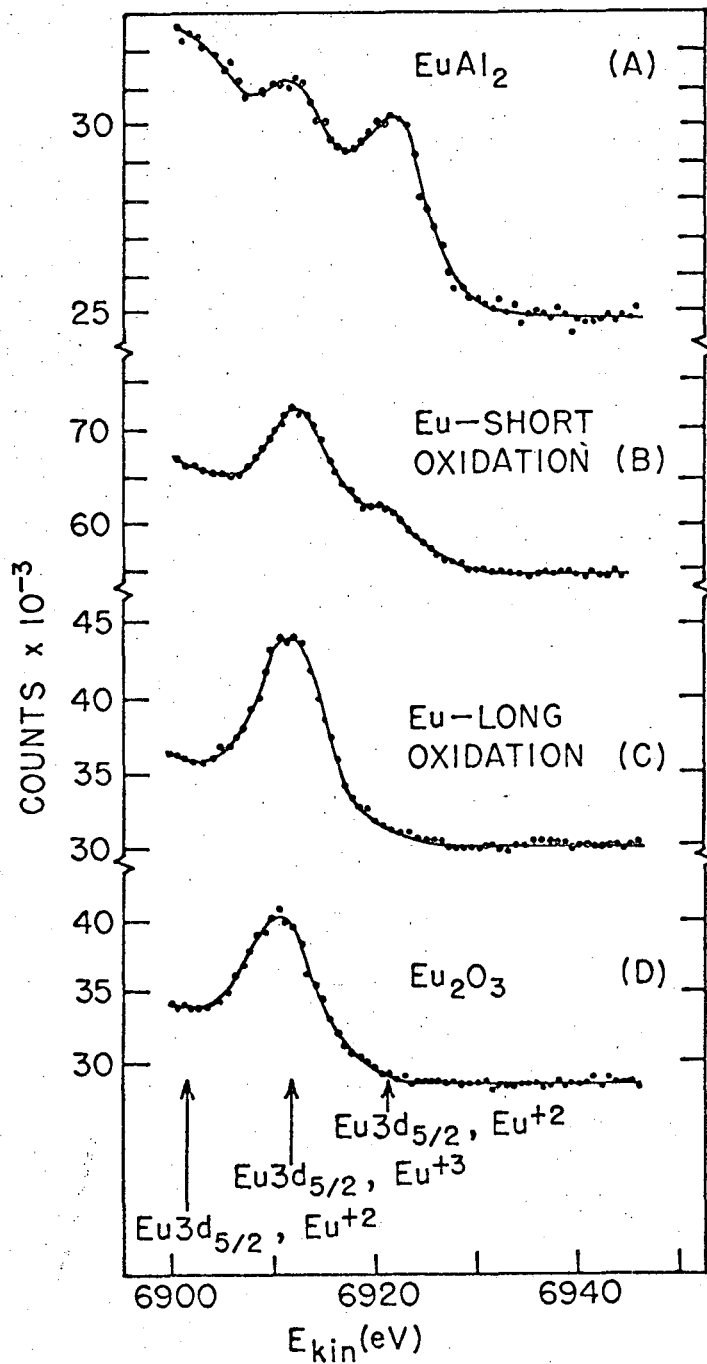
MUB 13961

Fig. 1



MUB13960 A

Fig. 2



XBL 672-632 A

Fig. 3

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

