

PHYSICAL REVIEW LETTERS

VOLUME 21

14 OCTOBER 1968

NUMBER 16

SPECTROSCOPY OF INNER ATOMIC LEVELS: ELECTRIC FIELD SPLITTING OF CORE $p_{3/2}$ LEVELS IN HEAVY ATOMS*

T. Novakov† and J. M. Hollander

Lawrence Radiation Laboratory, University of California, Berkeley, California 94720
(Received 1 August 1968)

Splittings of atomic core $p_{3/2}$ levels caused by internal electric field gradients have been observed in compounds of Th, U, and Pu by means of photoelectron and internal-conversion spectroscopy. The magnitude of the splitting varies with the element and specific compound examined, and it may be considerably enhanced by application of a strong external field.

Until recently, only limited study has been made of the chemical aspects of inner, or core, atomic levels because, in part, of a scarcity of experimental tools for probing these levels in detail.

Of the observable phenomena that relate directly to the structure of inner levels, the following are most significant: (I) x-ray absorption and emission, (II) internal conversion of nuclear radiation, and (III) photoelectron emission. From x-ray spectroscopy (I), chemical shifts in the x-ray absorption edges and emission lines have been found.¹ A considerable amount of detailed information about the interactions of core levels with the atomic environment is now being provided by use of techniques II²⁻⁴ and III.⁵⁻⁷ In the latter cases, high-resolution electron spectroscopy is proving to be a valuable tool.

Splittings of the outer (optical) levels induced by external fields and by crystal fields have long been known, but little is known about such splittings of core levels. The purpose of this Letter is to describe several experiments by which splittings of inner $p_{3/2}$ levels of heavy-element atoms have been observed. These observations were made under three different experimental

situations, involving measurement of (a) photoelectron spectra excited by low-energy x rays, (b) internal-conversion electron spectra from radioactive sources, and (c) internal-conversion spectra from radioactive sources exposed to an external electric field.

The atomic level energy E_b (or electron binding energy) is related by energy conservation to the kinetic energy of an emitted atomic electron by the following equation:

$$E_b = E_{\text{exc}} - E_{\text{kin}} - \varphi,$$

where E_{exc} is the excitation energy ("gamma-ray" energy in the case of internal conversion and x-ray energy in the case of photoelectron emission) and E_{kin} is the kinetic energy of the emitted electron. φ is a small correction for the work function of the spectrometer material.

Of the experimental situations mentioned, photoelectron spectroscopy offers the possibility to investigate atomic level energies with the highest resolution. This is so because of the lower kinetic energies associated with photoelectron emission than are normally encountered with internal conversion. In the work reported here, Mg $K\alpha$ x rays (1254 eV) were used as the excitation

source, and a 50-cm iron-free magnetic spectrometer was used to record the photoelectron spectra. This system produced lines with full width at half-maximum of about 2 eV.

We have studied the photoelectron spectra from metallic sources of tantalum, platinum, gold, thorium, uranium, and plutonium, as well as from some compounds of thorium and uranium. Figure 1 shows some portions of the spectra produced from targets of U metal, Th metal, and UO_3 irradiated with Mg $K\alpha$ radiation. In these spectra, photolines from N_{VI} ($4f_{5/2}$), N_{VII} ($4f_{7/2}$), O_{III} ($5p_{3/2}$), O_{IV} ($5d_{3/2}$), and O_V ($5d_{5/2}$) levels are shown. The O_I ($5s_{1/2}$) and O_{II} ($5p_{1/2}$) lines are apparently only very weakly excited and were not clearly observed in our spectra.

It was found that all of these lines have a normal shape except the O_{III} , which shows a composite structure. The shape of the O_{III} line varies with the particular compound examined, but in all cases a splitting was seen. The magnitude of the splitting is evidently chemistry dependent. In the case of uranium, the sources used were the metal, UO_2 , UO_3 , uranyl nitrate, and uranyl acetate; of these, the largest splitting (10 eV) was found with the uranyl acetate, the smallest

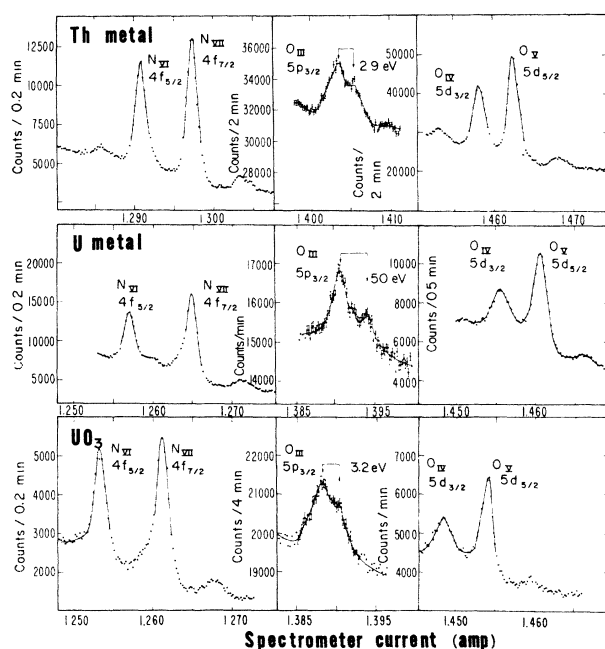


FIG. 1. Portions of the photoelectron spectra from targets of thorium metal, uranium metal, and UO_3 irradiated with Mg $K\alpha$ radiation. N_{VI} , N_{VII} , O_{III} , O_{IV} , and O_V photolines are shown. These data were recorded with the Berkeley iron-free spectrometer.

(3 eV) with UO_2 . With plutonium metal, the separation between the main components appeared to be about 16 eV.

In contrast to the results with thorium, uranium, and plutonium, the targets of tantalum, platinum, and gold metals produced no evidence for complexity in the O_{III} line or in any other line.

In order to eliminate the possibility that the observed complexity of the O_{III} lines could be caused by Auger lines of coincidentally similar energy, the measurements on the uranium compounds were repeated with Al $K\alpha$ radiation. The previous results were confirmed. The measurements were also repeated with materials of different origin to minimize the probability of interfering lines arising from impurities.

These results, which we interpret as evidence for level splitting, are believed to be distinct from the chemical-shift effect that is well known in photoelectron spectroscopy.⁵⁻⁷ The latter, which arises from small changes in the binding energies of electrons in different chemical environments, affects all core levels by about the same amount.⁶

Other evidence for the splitting of the $p_{3/2}$ level in heavy elements has been found in internal-conversion spectroscopy [situations (b) and (c) mentioned above]. In a study of the internal conversion lines of the 7.85-keV transition from the decay of 2.3-day ^{239}Np , Novakov et al.⁸ observed that the shapes of the O_{II} and O_{III} lines are different, with evidence of structure in the O_{III} line. A portion of the spectrum is shown in Fig. 2. The half-width of the O_{II} line is 38 eV, and we estimate that a splitting of about 15 eV in the O_{III} line could cause the observed shape. The

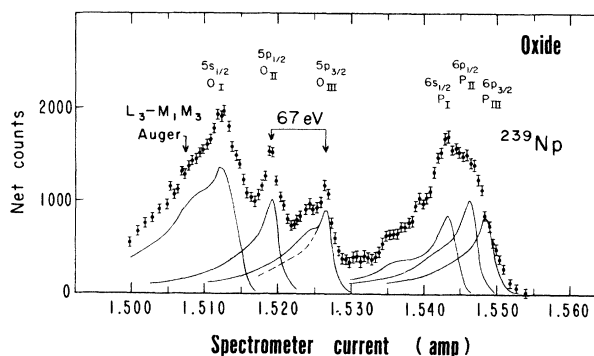


FIG. 2. O and P internal conversion lines of the 7.85-keV nuclear transition in ^{239}Pu following the decay of ^{239}Np . Solid lines represent the graphically resolved line shapes. These data were recorded with the Berkeley iron-free spectrometer.

difference in natural width between the O_{II} and O_{III} lines, probably less than 2 or 3 eV,⁹ is too small to be responsible for this effect.

In another related experiment, Novakov and Hollander¹⁰ were able to induce changes in the shapes of internal conversion lines from $p_{3/2}$ levels by placing radioactive sources in a high external electric field. The conversion lines were measured with the same spectrometer system as the photoelectron lines discussed above. With a ^{233}Pa source in a field of about 10^6 V/cm, the L_{III} conversion line of a 40.4-keV transition showed a satellite (or shoulder) on the low-energy side of the main component, while the L_I and L_{II} lines showed no structure. Because of the relatively large instrumental linewidth in this situation, about 100 eV for the L_{II} line, the satellite was not completely resolved from the main peak.

Similar experiments were subsequently performed by Novakov and Janičijević¹¹ with ^{239}Np sources prepared in different chemical forms, and it was found that a satellite on the L_{III} line of a 57.2-keV transition was induced by the field, with a separation of about 100 eV from the main component, while the L_{II} line remained essentially unchanged. The relative intensity of the satellite portion of the line depended on the field strength and also upon the chemical form of the source. The satellites were observed with chloride and oxide sources but not with hydrated oxide sources, as can be seen from Fig. 3.

Thus, the results of the experiments described here indicate that a splitting or energy shift takes place in $p_{3/2}$ levels of the elements mentioned, under the combined influence of external and internal fields, or of the latter alone. The

effect appears to be unique to the $p_{3/2}$ levels and has not been seen either in the $p_{1/2}$ level or in the d levels. The mutual consistency of the results from the several experiments, involving completely different circumstances, is illustrated by the fact that the observed splitting energy of the $5p_{3/2}$ level in plutonium is of similar magnitude whether obtained from internal conversion (≈ 15 eV) or from photoelectron emission (≈ 16 eV).

Although a mechanism to account for these observations has not been established with certainty, it is probable that the splitting of the core $p_{3/2}$ levels is caused by an effective electric field gradient in the interior of the atom. The origin of this field gradient may be related to the factors responsible for the field gradient at the nucleus (Sternheimer effects). On the other hand, a more direct effect arising from chemical bonding may be responsible for the field at the $5p$ shell. If, for example, the symmetries of the $6p$ or other outer orbitals in the actinides are altered because of their participation in chemical bonding, a gradient might be felt at the $5p$ levels that is large enough to split the $m = \pm\frac{1}{2}$ and $m = \pm\frac{3}{2}$ substates of the $5p_{3/2}$ level by the amount observed.

The fact that the splitting was seen with Th metal requires comment. Thorium metal has a cubic structure, which would not produce quadrupole fields in the interior of the crystal, but substantial fields might be expected near the surface in the case of our samples since no special precautions were taken to prevent the formation of surface oxide layers. This is an important consideration in x-ray photoelectron spectroscopy with solids, as the emitted photoelectrons are produced in a thin layer from the surface to a

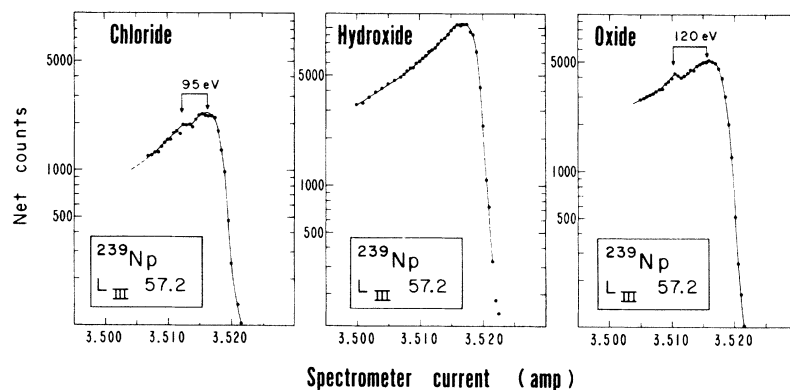


FIG. 3. L_{III} internal conversion line of the 57.2-keV nuclear transition from ^{239}Np sources prepared in different chemical forms and exposed to a strong electrostatic field. These data were recorded in Belgrade, and the figure has been modified slightly from Ref. 11.

depth of not more than about 100 \AA .⁵ As mentioned above, splittings were not observed with metallic gold, platinum, or tantalum, but in these cases there is much less surface oxide present. It is obviously of interest to repeat and extend these measurements under controlled chemical conditions.

The application of an external electric field provides an additional contribution to the internal field gradient through induced polarizations of the electron shells. In this connection we note that with the external field the splitting observed in the deep-lying $2p$ level was as large as 100 eV , which is an order of magnitude greater than that seen in the $5p$ level without the external field. It is interesting that the external field was not effective with a hydrated-oxide source [Fig. 2(b)], in which the water molecules can act as an electrostatic shield, but became effective with the same source after it was ignited to the oxide [Fig. 2(c)].

The authors are very grateful to Professor D. A. Shirley for his interest and helpful comments.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

†On leave from the B. Kidrich Institute, Belgrade, Yugoslavia.

¹A. Faessler and M. Goehring, *Naturwiss.* **39**, 169 (1952).

²J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman, and G. T. Emery, *Phys. Rev. Letters* **17**, 809 (1966).

³T. A. Carlson, P. Erman, and K. Fransson, *Nucl. Phys.* **A111**, 371 (1968).

⁴J. A. Cooper, J. M. Hollander, and J. O. Rasmussen, *Phys. Rev. Letters* **15**, 680 (1965); J. A. Cooper, thesis, University of California Lawrence Radiation Laboratory Report No. UCRL-16910, September, 1966 (unpublished).

⁵K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S.-E. Karlsson, I. Lindgren, and B. Lindberg, *Electron Spectroscopy for Chemical Analysis, Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy* (Almqvist and Wiksells Publishing Company, Stockholm, Sweden, 1967).

⁶C. S. Fadley, S. B. M. Hagström, J. M. Hollander, M. P. Klein, and D. A. Shirley, *Science* **157**, 1571 (1967); C. S. Fadley, S. B. M. Hagström, M. P. Klein, and D. A. Shirley, *J. Chem. Phys.* **48**, 3779 (1968).

⁷J. M. Hollander, D. N. Hendrickson, and W. L. Jolly, to be published, and University of California Lawrence Radiation Laboratory Report No. UCRL-18298, July, 1968 (unpublished).

⁸T. Novakov, R. Stepić, and P. Janičijević, unpublished results.

⁹F. K. Richtmyer, S. W. Barnes, and E. Romberg, *Phys. Rev.* **46**, 843 (1934).

¹⁰T. Novakov and J. M. Hollander, *Phys. Letters* **13**, 301 (1964).

¹¹T. Novakov and P. Janičijević, *Z. Physik* **205**, 359 (1967).

ENERGY ANALYSIS OF ELECTRONS FROM PENNING IONIZATION PROCESSES

V. Fuchs and A. Niehaus

Physikalisches Institut der Universität Freiburg, Freiburg, Germany

(Received 22 July 1968)

The energy of electrons released in collisions of metastable rare gas atoms with various gases is measured by means of a retarding potential field. The energy distributions obtained show a marked influence of the interaction forces between the colliding particles.

Measuring the energy of electrons ejected in Penning ionization processes¹

$$A^* + B \rightarrow A + B^+ + e^-(E_{el}) \quad (1)$$

can yield information about the energy of ionic states $E_i(B^+)$. In contrast to the photoionization, optically forbidden transitions $B \rightarrow B^{*+}$ can be studied. The first experimental investigations in this field of "Penning-ionization electron spectroscopy" were done by Cermák.²

Another important difference between (1) and photoionization is the fact that the energy rela-

tion $E_{el} = E_{ex}(A) - E_i(B^+)$, where $E_{ex}(A)$ is the excitation energy of A , is only an approximation. In principle it must be expected that the relative kinetic energy of the system is different before and after the ionization process. In other words, the relation should be

$$E_{el} = E_{ex}(A) - E_i(B^+) + \Delta E, \quad (2)$$

where ΔE can be positive or negative. If ΔE is positive and greater than the relative kinetic energy of the neutral system at infinity, associa-