Photoionization Experiments with an Atomic Beam of Tungsten in the Region of the $5p$ and $4f$ excitation

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(Received 31 January 1995)

An atomic beam of tungsten and photoexcitation with monochromatized synchrotron radiation were used to measure the first photoion yield spectra of W^+ and W^{2+} in the region of 30–60 eV. The comparison with calculated photoionization cross sections shows that the resonance structure can be explained by discrete $5p \rightarrow 5d$, $6s$ and $4f \rightarrow 5d$ transitions if one takes into account the thermal population of the initial states $5d^4 6s^2\,{}^5D_{0,1,2,3,4}$ and $5d^5\,6s\,{}^7S_3$.

PACS numbers: 32.80.Fb, 32.80.Hd

Whereas for the elements of the iron group ($3d$ transition metals) atomic photoionization studies in the vacuum ultraviolet (VUV) region were reported in several publications, there are only a few papers on the transition metals of the ($4d$) palladium or ($5d$) platinum group [1]. The simple reason is the difficulty in the evaporation of these refractory elements: tungsten, for example, the most prominent member of the $5d$ transition metals, requires temperatures of about 3200 K. Although this property is responsible for the technological importance of tungsten in high temperature applications, it is a severe handicap for the production of free atoms in a vapor column or an atomic beam. Therefore, usually techniques other than the thermal evaporation from the metal are used to produce free tungsten atoms. So the dissociation of compounds like WF_6 in a hot plasma [2] or the sputtering technique [3,4] were applied in experiments for the determination of oscillator strengths in the optical region. In the VUV region the first photoabsorption experiments with atomic tungsten recently were performed with the dual laser plasma technique, where both the absorbing plasma and the VUV continuum emitting plasma are produced by the high power beams of a synchronized twin-laser system focused on solid targets [5].

All these methods utilize plasma interaction techniques, which imply the production of a large amount of charged particles. The coexistence of neutrals and charged particles in the gas target, however, can be unfavorable for photoionization experiments of neutral atoms if one concentrates on the investigation of the decay process by the observation of the resulting photoions. Especially in the region of autoionizing resonances, photoion spectroscopy has proved as a very suitable method to obtain a deeper insight in the complex dynamics of inner-shell processes [6]. For atomic tungsten strong resonances were observed in the absorption experiments with the dual laser plasma technique [5] in the region between 30 and 60 eV, which were attributed to transitions of $5p$ electrons into unoccupied $5d$ orbitals. From recent calculations of the photoionization cross section based on the formalism of many-body perturbation theory [7], one expects similar resonances due to the $4f \rightarrow 5d$ transitions in the region between 28 and 35 eV. In order to study these resonances with the method of photoion spectroscopy, we produced an atomic beam of tungsten by thermal evaporation from the metal. The necessary temperatures of about 3200 K obviously prevent the use of standard atomic beam technique. Heating by electron impact, for example, resulted in a nontolerable background of charged particles in the beam, which could not be sufficiently reduced by electric fields. We, therefore, used the direct heating of thin wires (0.5 mm inner diam, $I \simeq 25$ A) just below the melting point with an emitting area of about 2 mm^2 placed on the axis of the atomic beam [8,9]. A rough estimation of the particle density in the interaction region of atomic and photon beam from the evaporation rate yielded $<10^9$ particles/cm^3. Compared with the typical value of 10^{11} particles/cm^3 of gas phase experiments in the VUV region, this value represents a challenge to the experimentalist. Nevertheless, this method offers the possibility to produce a "clean" beam of atomic tungsten and can also be used for other refractory elements like tantalum, iridium, or rhenium.

The inner-shell excitation of the tungsten atoms was performed with the monochromatized synchrotron radiation of the electron storage ring BESSY in Berlin. The photon beam with an energy resolving power of $E/\Delta E \simeq 120$ was focused on the atomic beam, and the photoions W^+ and W^{2+} were detected by a standard time-of-flight technique with a pulsed electric field [10]. Special care was taken to control the detection efficiency for a differently charged ions.

The photoion yield spectra of W^+, W^{2+}, and the sum ($W^+ + W^{2+}$) in the range of 30–60 eV are shown in Fig. 1. A considerable background of stray ions from residual gas was found, which was quantitatively measured at a few fixed photon energies; it is expected to add a slowly varying contribution to the signal of the order of 1000–2000 counts on the given scale. The background was linearly approximated and subtracted. This procedure

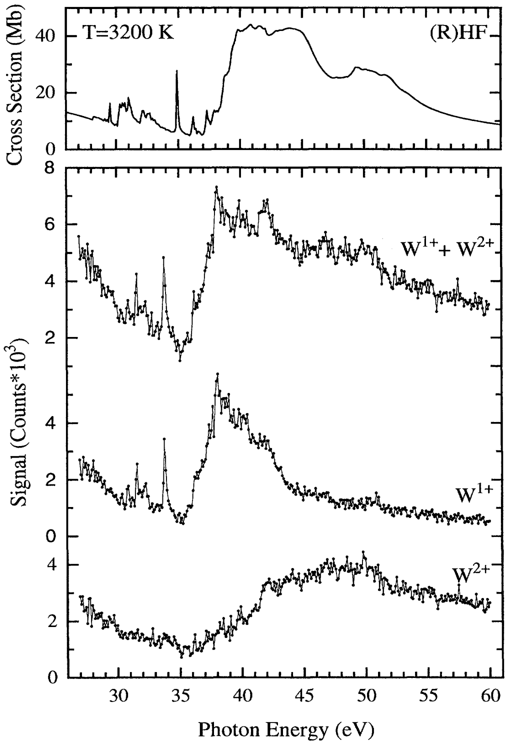

FIG. 1. Partial photoion yields of W^+, W^{2+} and total photoion yield ($W^+ + W^{2+}$) in the region of $4f$ and $5p$ excitations. The photoabsorption cross section on top of the figure is the weighted sum of the different contributions in Fig. 3.

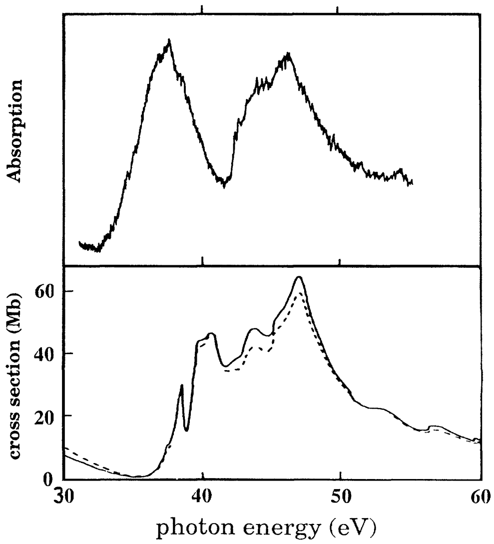

FIG. 2. Top: photoabsorption of tungsten measured with dual laser plasma technique [5]. Bottom: photoabsorption cross section calculated with MBPT for the $^5D_0$ ground state of tungsten [7].

leaves an estimated uncertainty of 200–300 counts offset, especially in the low energy regime. The smallness of the signal excluded the use of filters for high order suppression of the monochromator. We estimate a contribution of signal due to higher spectral orders of about 500 counts at 30 eV decreasing to about 200 counts at 50 eV for the total photoion yield. Since these errors produce only a smooth offset, the sum of the W^+ and W^{2+} signals in Fig. 1 should resemble all important features of the total photoionization cross section.

The main features of the ($W^+ + W^{2+}$) signal are a broad Fano-type resonance centered at 38 eV with superimposed maxima at 42, 47, and 50 eV, some sharper structures at about 32 eV, and a distinct sharp resonance at 34 eV. For comparison the results of the absorption experiments of Costello *et al.* [5] and the calculated cross section of Boyle, Altun, and Kelly [7] starting from the ground state $5d^4 6s^2\,{}^5D_0$ are shown in Fig. 2. In the absorption spectrum there are two dominant resonances, where the first one centered at 37.5 eV may be identified with the corresponding photoion signal at 38 eV. On the other hand, there are no prominent sharper structures between 30 and 35 eV, and the second dominant broad peak at about 46 eV has no counterpart in the photoion signal. The comparison with the calculated cross section based on many-body perturbation theory [7] shows considerable differences. The pronounced minimum at 35.5 eV does coincide with the photoion signal, but the other features cannot be confirmed by our experimental data. This, however, is not surprising because the experimental results consist of the sum of excitation processes from several fine structure levels, whereas the calculated cross section shows the excitation from the ground state $^5D_0$.

To clarify these discrepancies we have performed relativistic Hartree-Fock calculations. We were confronted with a large number of closely spaced final states. Therefore we extended the method of separate Fano resonances previously applied to Pt [11] to the formalism of overlapping resonances interacting with many continua [12].

For the discrete $4f$ and $5p$ excitations the following initial and final state configurations were taken into account

$$4f^{14}5p^6(5d,6s)^6 \longrightarrow 4f^{14}5p^5(5d,6s)^7$$
$$\text{and } 4f^{13}5p^6(5d,6s)^7.$$

The continua were restricted to the configurations $4f^{14}5p^6(5d,6s)^5\,\varepsilon(p,f)$ with the dominant contribution of the εf continua. Considering the high temperatures we used as initial states next to the ground state $5d^4 6s^2\,{}^5D_0$ the other four $^5D_{1,2,3,4}$ states of the configuration $5d^4 6s^2$ and the $^7S_3$ state of the configuration $5d^5 6s$ (all notations according to Ref. [13]). The resulting photoionization cross sections for these six initial states are depicted in Fig. 3. The sum of the different contributions according to the thermal population of 3200 K is shown in the top of Fig. 1. Although the very large number of final states

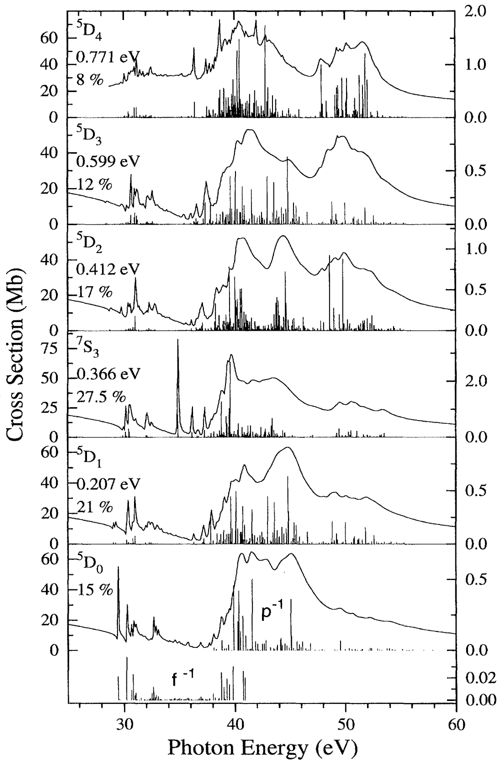

FIG. 3. Photoabsorption cross section obtained within the framework of overlapping resonances interacting with many continua [12]. The vertical lines below each curve indicate the strength of the resonances. For the $^5D_0$ ground state, as an example, the resonances corresponding to final states with f holes and p holes are given separately. The eye-catching sharp resonance at 35 eV from the $5d^56s\,^7S_3$ initial state is a $5p \rightarrow 6s$ excitation to $5p^55d^56s^2\,^7P_4$.

does not allow a listing of all the 5096 resonances one can distinguish certain characteristic features, which can also be identified in the photoion signals:

(a) A group of smaller resonances between 30 and 33 eV, which can be attributed to $4f \rightarrow 5d$ transitions.

(b) A prominent sharp resonance at 35 eV in the contribution of the $5d^56s\,^7S_3$ initial state. This resonance can be attributed to a $5p \rightarrow 6s$ transition into the unfilled $6s$ subshell and is analogous to the $3p^63d^54s\,^7S_3 \rightarrow 3p^53d^54s^2\,^7P_4$ transition in Cr. In the periodic table, Cr occupies the same position in the $3d$ group as W in the $5d$ group with the difference that the $^7S_3$ is the ground state of Cr.

(c) There is a large group of broader resonances ($\Gamma \sim 1$ eV) between 38 and 53 eV, which can be attributed to $5p \rightarrow 5d$ transitions. The sharper features ($\Gamma \sim 0.1$ eV) between 38 and 41 eV are due to $4f \rightarrow 5d$ transitions.

If one compares the contributions of the different initial states one can see that the resonances at lower photon energies between 38 and 45 eV are more favored by the lower energy initial states, whereas the group between 48 and 53 eV can be related to the higher energy initial states. Therefore one can try to explain the differences between the photoion signals and the absorption spectrum with the dual laser plasma technique [5]: If in the laser-produced plasma there is a large number of atoms in higher metastable states then the $4f \rightarrow 5d$ and $5p \rightarrow 6s$ contributions may be masked by the $5p \rightarrow 5d$ resonances. The two groups of the $5p \rightarrow 5d$ resonances are split by a distance of about 8 eV, which is in fair agreement with the $5p$ spin-orbit splitting. Therefore one may attribute the first group to $5p_{3/2}$ transitions and the second group to $5p_{1/2}$ transitions. In the simplified picture of pure jj coupling the $5p_{1/2}$ transitions are forbidden to a $(5d_{3/2})^4$ configuration. The actual states obviously are not pure jj states [e.g., the ground state consists of $(5d_{3/2})^4$ and $(5d_{3/2})^2(5d_{5/2})^2$ components [7]] but the dominance of the $(5d_{3/2})^4$ components in the lower states explains the preference of the $5p_{3/2}$ transitions from these states.

Because of the experimental difficulties mentioned above, a quantitative evaluation of the W^+ and W^{2+} branching ratio was not possible. The increase of W^{2+} above 35 eV may be attributed to the opening of Auger decay channels after direct $4f$ or $5p$ ionization:

$$4f^{14}5p^6(5d,6s)^6 \longrightarrow 4f^{13}5p^6(5d,6s)^6\,\varepsilon l \longrightarrow 4f^{14}5p^6(5d,6s)^4\,\varepsilon l, \varepsilon' l',$$

$$4f^{14}5p^6(5d,6s)^6 \longrightarrow 4f^{14}5p^5(5d,6s)^6\,\varepsilon l \longrightarrow 4f^{14}5p^6(5d,6s)^4\,\varepsilon l, \varepsilon' l'.$$

A very weak modulation of the W^{2+} signal can be observed at the position of the W^+ maximum at 42 eV, and the features in the 47–50 eV range seem to stem mainly from the corresponding maxima in the W^{2+} signal. A possible explanation of these features could be a two-step decay process of $5d_{3/2}$ resonances by the spin-flip mechanism $5p_{1/2} \rightarrow 5p_{3/2}$ followed by Auger decay.

In conclusion, we have observed the first photoion spectra of free tungsten atoms in the region of 30–60 eV in spite of the severe difficulties in the handling of atomic tungsten. Tentative assignments of the main excitation and decay processes were obtained with aid of *ab initio* calculations.

The authors thank the BESSY staff for assistance. The financial support from the BMFT is gratefully acknowledged.

[1] B. Sonntag and P. Zimmermann, Rep. Prog. Phys. **55**, 911 (1992).
[2] J.E. Clawson and M.H. Miller, J. Opt. Soc. Am. **63**, 1598 (1973).
[3] P.S. Ramanugam, Phys. Rev. Lett. **39**, 1192 (1977).
[4] P. Hannaford and R.M. Lowe, J. Phys. B **14**, L5 (1981).
[5] J.T. Costello, E.T. Kennedy, B.F. Sonntag, and C.L. Cromer, J. Phys. B **24**, 5063 (1991).

[6] Ch. Dzionk, W. Fiedler, M. v. Lucke, and P. Zimmermann, Phys. Rev. Lett. **62**, 878 (1989).
[7] J. Boyle, Z. Altun, and H. P. Kelly, Phys. Rev. A **47**, 4811 (1993).
[8] W. M. Doyle and R. Marrus, Nucl. Phys. **49**, 449 (1993).
[9] M. Kwiatkowski, G. Micali, K. Werner, M. Schmidt, and P. Zimmermann, Z. Phys. A **304**, 197 (1982).
[10] D. M. P. Holland, K. Codling, J. B. West, and G. V. Marr, J. Phys. B **12**, 2465 (1979).
[11] P. Sladeczek, M. Martins, M. Richter, K.-H. Selbmann, and P. Zimmermann, J. Phys. B **27**, 4123 (1994).
[12] F. H. Mies, Phys. Rev. **175**, 164 (1968).
[13] C. E. Moore, Atomic Energy Levels, NBS Circular No. 467, Vol. III (1971).