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Diagnostics of the plasma parameters based on the K X-ray line positions for various 4d and 4f metals

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Abstract. This paper shows the theoretical predictions of the outer-shell ionization effect on the positions of $K\alpha_{1,2}$, $K\beta_{1,3}$, and $K\beta_2$ X-ray lines for some 4d-transition metals (molybdenum and palladium) and 4f rare-earth elements (dysprosium and ytterbium). The ionization energy shifts have been evaluated using the multiconfiguration Dirac-Fock method, containing Breit interaction and quantum electrodynamic (QED) corrections. The presented results are important for obtaining the information about some parameters of plasma generated by different sources, especially by pulsed power machine and short-pulse lasers.

Key words: plasma diagnostic • outer-shell ionization • K X-ray lines

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Introduction

The outer-shell ionization of various elements in plasmas is mainly a function of the plasma temperature and density. Therefore, it can affect the energy positions and shapes of the characteristic X-ray lines in radiation emitted from plasmas, what should be helpful in plasma diagnostics. However, until 2011, the knowledge concerning the influence of outer-shell electron stripping on the K, L, and M X-ray lines, based on the results of systematic theoretical studies has not been hitherto known in scientific literature. Lack of this knowledge caused serious difficulty in the interpretation of the complex X-ray registered spectra structures emitted by mid-Z and heavy elements in the hot plasma in recent years (see e.g., [1]). This situation has encouraged us to perform the series of detailed theoretical studies concerning the influence of outer-shell electron stripping on the K, L, and M X-ray lines for many elements [2–11].

Part of our previous theoretical results has been already used in order to obtain the information about some of the plasma parameters. The value of energy shift for strong $K\alpha_2$ line of iridium registered using filter (i.e., K-edge filter) for iridium plasma generated by the Naval Research Laboratory's (NRL) Gamble II pulsed power machine, using plasma-filled rod pinch (PFRP) diode allowed the precise determination of ionization level for iridium ($q \sim 17$) and the electron temperature of iridium plasma (~60 keV) [4, 5, 9]. Recently [7], on the basis of our theoretical studies has been shown the reliable

interpretation of not explained earlier the mystery of ytterbium's Kβ line (the negative ionization energy shift of this line) emitted from the plasma produced also by the PFRP diode. Moreover, the ionization distribution has been evaluated for the first time [6] by decomposition of the registered (broad, asymmetric, and shifted) $L\beta_2$ line shape into the theoretical predictions, corresponding to different degrees of ionization. It is worth underline that this distribution has been evaluated without using any theoretical models (like hydrodynamic, atomic kinetics, and radiative simulation codes).

The main aim of this work has been to provide an exhaustive set of theoretical predictions about the effect of outer-shell electron stripping on the positions of the K X-ray lines for some 4d-transition and 4f rare-earth elements, which can be of vital importance in designing new diagnostics of plasma parameters by the interpretation of X-rays spectra emitted from the plasma generated in various sources.

To provide a sufficient accuracy of the performed calculations, it was essential to use the relativistic multiconfigurational Dirac-Fock (MCDF) method, including Breit interaction and quantum electrodynamics (QED) corrections. The following prediction of energy shifts has been determined with high accuracy, that is, of the order of 0.05–0.1 eV [12].

Research methodology

Our presented results have been obtained using the MCDF method, which is one of the main theoretical tool used to study the X-ray spectra structure. This method was primarily developed by Grant (and his co-workers) and presented in detail in many previous works (e.g., [12–15]). In the MCDF code, the relativistic Hamiltonian, H for N-electron system is given by:

$$H = \sum_{i=1}^{N} h_{\mathrm{D}}(i) + \sum_{i<j}^{N} \frac{1}{r_{ij}} \tag{1}$$

Here, $h_{\mathrm{D}}(i)$ represents the Dirac operator for the i-th electron. The term C_{ij} is defined as the sum of two operators: the Coulomb operator and transverse Breit operator. In the MCDF code, the atomic state function, with the total angular momentum J and parity p is expressed by:

$$\Psi_S(J^p) = \sum_m c_m(s)\, \Phi\left(\gamma_m J^p\right) \tag{2}$$

where, $\Phi(\gamma_m J^p)$ are the configuration state functions (CSFs) composed by one-electron Dirac spinors, the term $c_m(s)$ describes the configuration mixing coefficients for state s, and next γ_m means all needed information to clearly define a CSF.

It should be noted that in MCDF calculations, it was necessary to take into account not only the Breit correction to Coulomb repulsion operator, but also the QED corrections (i.e., self-energy and vacuum polarization) and a finite size nucleus model, in order to obtain a reliable description of the X-ray spectra structure for selected 4d-transition metals and 4f rare-earth elements.

Results and discussion

Figures 1–4 present the theoretical predictions of ionization energy shifts obtained systematically for various K X-ray lines as a function of outer-shell electron stripping (i.e., as electrons are removed from the ion in order of their binding energy) for 4d-transition metals [Mo (Z = 42) and Pd (Z = 46)] and for 4f rare-earth elements [Dy (Z = 66) and Yb (Z = 70)]. All energy shifts have been evaluated using the MCDF method. It is worth noticing that in Figs. 1–4, various outer-shell ionization levels have been included. The results of our study indicate that the particular K X-ray lines are generally characterized by significantly different sensitivity to the outer-shell electron stripping.

Molybdenum and palladium ionization energy shifts

Figure 1 presents the energy shifts as a function of the ionization q, obtained by stripping of the outer-shell electrons in order of their binding energies, for the $K\alpha_{1,2}$ and $K\beta_{1,3}$ X-ray lines of molybdenum. All energy shifts have been evaluated with respect to the corresponding diagram line energies obtained for molybdenum's ground state electronic configuration, $[Kr]\ 4d^5 5s^1$.

As can be seen from Fig. 1, the energy shifts of $K\alpha_1(2p_{3/2} \rightarrow 1s)$ and $K\alpha_2(2p_{1/2} \rightarrow 1s)$ X-ray lines are insignificant for outer-shell ionization levels up to $q \sim 6$. From about $q \sim 6$, the $K\alpha_{1,2}$ energies start to slowly increase. The strongest growth we observe from about $q \sim 24$, up to 110 eV for the highest ionization degree ($q = 32$). Figure 1 also shows the ionization energy shifts of the $K\beta_1(3p_{3/2} \rightarrow 1s)$ and $K\beta_3(3p_{1/2} \rightarrow 1s)$ X-ray lines as a function of outer-shell electron stripping. One can notice very similar insensitivity for low outer-shell ionization as we notice for $K\alpha_{1,2}$ X-ray lines, above $q \sim 6$, the ener-

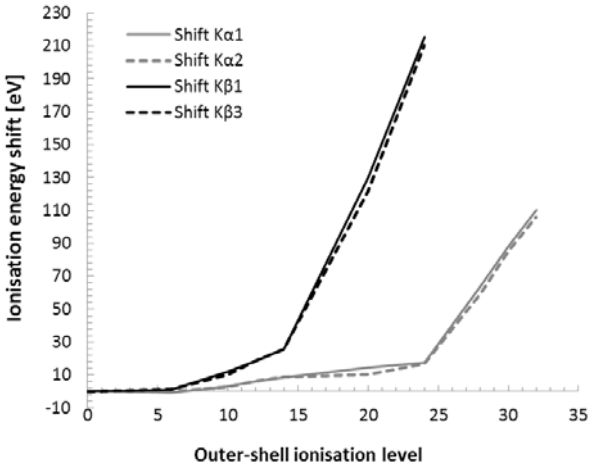

Fig. 1. Energy shifts for $K\alpha_{1,2}$ (grey solid and dashed) and $K\beta_{1,3}$ (black solid and dashed) lines as a function of outer-shell stripping of molybdenum, predicted by the MCDF calculations.

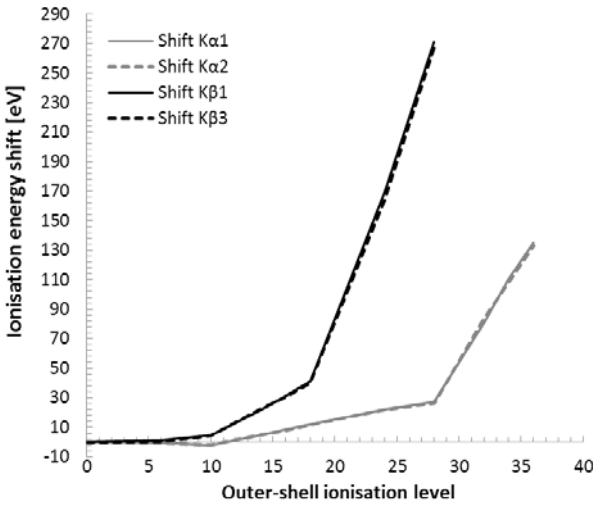

Fig. 2. Energy shifts for $K\alpha_{1,2}$ (grey solid and dashed) and $K\beta_{1,3}$ (black solid and dashed) lines as a function of outer-shell electron stripping of palladium, obtained by the MCDF calculations.

gies increase slowly, above $q \sim 14$, grow dramatically, and we achieve the values of 215 eV for the highest investigated value ($q = 24$).

Figure 2 presents the energy shifts of the $K\alpha_{1,2}$ and $K\beta_{1,3}$ X-ray lines of palladium also as a function of outer-shell electron stripping. The energy shifts have been calculated with respect to the corresponding diagram line energies obtained for the [Kr] $4d^{10}$ ground state electronic configuration of palladium. For almost all ionization degrees, the dependence between the energy shifts of $K\alpha_{1,2}$ and $K\beta_{1,3}$ lines of Pd is very similar to that observed for the same lines of Mo. The $K\alpha_{1,2}$ energies are insignificant for the outer-shell ionization levels up to $q \sim 10$. For higher ionization degrees ($q > 10$), these energies start to slowly grow, and the further outer-shell ionization (above $q \sim 28$) causes a strong increase, up to 135 eV for the highest examined value ($q = 36$). We can see from Fig. 2 that for $K\beta_1$ and $K\beta_3$ lines, the energy shifts are negligible for outer-shell ionization levels up to $q \sim 6$. From $q \sim 10$, the energies start to increase, and above $q \sim 18$, we can observe the rapid growth of $K\beta_1$ and $K\beta_3$ energy shifts, and we achieve the values of 271 eV for the highest ionization degree ($q = 28$).

Dysprosium and ytterbium ionization energy shifts

The ionization energy shifts of dysprosium obtained for the $K\alpha_{1,2}$, $K\beta_{1,3}$, and $K\beta_2$ X-ray lines as a function of electron stripping, for particular outer subshells have been shown in Fig. 3. All energy shifts have been evaluated with respect to the corresponding diagram line energies obtained for the [Xe] $4f^{10}6s^2$ ground state electronic configuration of this element. As can be seen, the removing of the valence 6s electrons does not practically affect the inner-shell $K\alpha_{1,2}$ transitions. In the next step, the removing of electrons from the 4f subshell causes a reduction in the $K\alpha_{1,2}$ energies (local minimum is about ~ -12 eV) and the negative energy shifts, called a red shift ($q \sim 12$). For ionization degrees between 12 and 30, when we start to remove electrons from 5p, 5s, and 4d subshells, the energy shifts slightly grow. The strongest increase of $K\alpha_1$ and $K\alpha_2$ energies we can observe for ion stages between 30 and 48 (when we are removing electrons from the 4p, 4s, and 3d subshells). Further ionization (removing electrons from the 3p and 3s subshells) causes a dramatic increase of $K\alpha_1$ and $K\alpha_2$ energies (up to 290 eV for $K\alpha_1$ X-ray lines and 258 eV for $K\alpha_2$ X-ray lines) for the highest ionization degree ($q = 56$).

For low ionization degrees, the dependence between $K\beta_{1,3}$ energy shifts of Dy is quite similar to that observed for the $K\alpha_{1,2}$ lines. The local minimum of the energy shift also appears at $q = 12$ (energy shift of $K\beta_{1,3} \sim -26$ eV, but is enhanced compared with the ~ -12 eV for $K\alpha_{1,2}$ energy shift). As can be expected, the $K\beta_{1,3}$ lines are more sensitive to outer-shell ionization (compared with more intense studied $K\alpha_{1,2}$ X-ray lines), so a lower ionization level is sufficient to have an effect on the line's energy. When we start to remove electrons from the 4d subshell, we can see a noticeable growth of $K\beta_{1,3}$ energies, and in the next step, the stripping of the valence 4p electrons causes a strongly and rapid increase of $K\beta_{1,3}$ energies (we achieve the value of 565 eV for the highest ionization degree $q = 48$). The removing of electrons from the 4d and 4p subshells affects the $K\beta_{1,3}$ lines more strongly than for the $K\alpha_{1,2}$ lines. It should be noted that the $K\beta_1$ and $K\beta_3$ lines (in Fig. 3) are shown together (as $K\beta_{1,3}$ lines), because the performed calculations cannot separate them. In case of Dy, 54 electrons are strongly bound in a Xe-like core, but the 12 electrons outside the core with an electronic configuration $4f^{10}6s^2$ have an open 4f shell, with many energy levels that are close together. So, the calculations must, therefore, consider many transitions with almost the same energies, and it becomes impossible to separate the $K\beta_1$ lines from the $K\beta_3$ lines.

Figure 3 also presents the ionization energy shifts of the $K\beta_2(4p_{3/2,1/2} \rightarrow 1s)$ X-ray lines as a function of outer-shell electron stripping for dysprosium. Separating the $K\beta_2^{I}$ lines from the $K\beta_2^{II}$ lines is also very difficult as in the case of the separation of $K\beta_1$ and $K\beta_3$ lines (for the same reason). It can be seen from Fig. 3 that the values of energy shifts of $K\beta_2$ lines are positive and their energies increase monotonically with q, and we achieve the value of 200 eV for the highest values ($q = 30$). These lines are the most sensitive on the outer-shell electron stripping (in reference to the studied $K\beta_{1,3}$ and $K\alpha_{1,2}$ lines for this element).

Figure 4 presents the energy shifts of $K\alpha_{1,2}$, $K\beta_{1,3}$, and $K\beta_2$ X-ray lines for ytterbium as a function of outer-shell stripping. All energies shifts have been calculated with respect to the energies of the corresponding diagram lines obtained for the [Xe] $4f^{14}6s^2$ ground state electronic configuration of Yb. For this element, for almost studied lines, we can notice a very similar situation to that observed for dysprosium (Fig. 3) when the same subshell is being ionized. As can be seen from Fig. 4, the energy shifts are insignificant for the lowest outer-shell ionization levels, up to $q \sim 2$. The removing of the

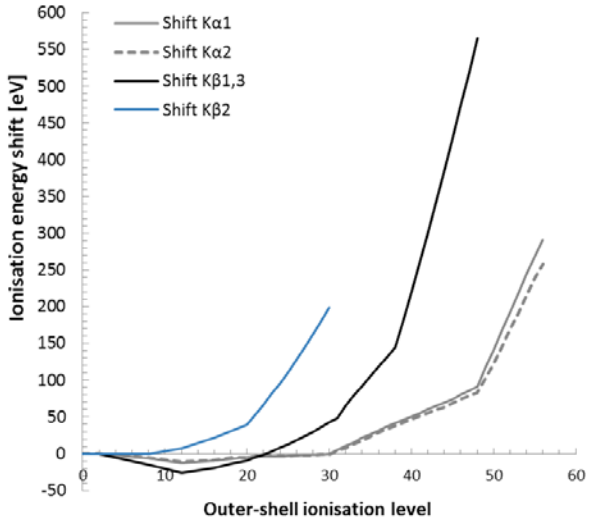

Fig. 3. Energy shifts for $K\alpha_{1,2}$ (grey solid and dashed), $K\beta_{1,3}$ (black solid), and $K\beta_2$ (blue solid) lines as a function of outer-shell stripping of dysprosium, predicted by the MCDF calculations.

electrons from the 4f subshell causes a reduction in the $K\alpha_{1,2}$ and $K\beta_{1,3}$ energies, and the negative energy shift, called a red shift. The local minimum of energy shift appears for ionization degree $q = 16$ (the value of energy shifts for $K\alpha_{1,2}$ is about ~ -18 eV, and the value of energy shifts for $K\beta_{1,3}$ is about ~ -37 eV), but the decrease of energies is slightly longer than for dysprosium, because ytterbium has four electrons more. Above $q \sim 16$, the $K\alpha_{1,2}$ and $K\beta_{1,3}$ energies start to increase slowly (when we remove electrons from the 5p, 5s, and 4d subshells), and above $q \sim 34$, these energies grow much more strongly (when we start to remove electrons from the 4p, 4s, and 3d subshells). From $q \sim 42$, the $K\beta_{1,3}$ energies increase dramatically (up to 644 eV for $K\beta_1$ and up to 600 eV for $K\beta_3$ X-ray lines) for the highest investigated value ($q = 52$) and above $q \sim 52$, the $K\alpha_{1,2}$ energies rapidly grow (up to 325 eV for $K\alpha_1$ and up to 284 eV for $K\alpha_2$ X-ray lines) for the highest ionization degree ($q = 60$).

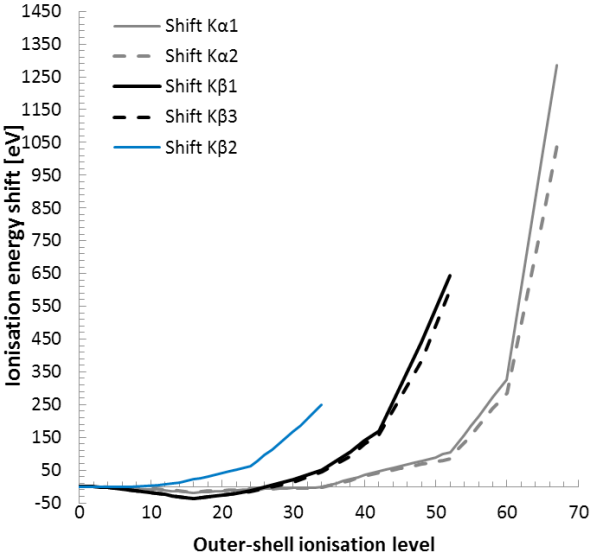

Fig. 4. Energy shifts for $K\alpha_{12}$ (grey solid and dashed), $K\beta_{1,3}$ (black solid and dashed), and $K\beta_2$ (blue solid) lines as a function of outer-shell stripping of ytterbium, obtained using the MCDF calculations.

It is worth emphasizing that the $K\beta_{1,3}$ X-ray lines are more sensitive on the other-shell stripping than $K\alpha_{1,2}$ X-ray lines.

As can be seen from Fig. 3, the ionization energy shifts of $K\beta_2$ X-ray lines increase monotonically with q, and we achieve the value of 250 eV for the highest ionization degree ($q = 34$). In the case of ytterbium, we can notice that the $K\beta_2$ X-ray lines are the most sensitive on the outer-shell electron stripping than the previous lines. Separating the $K\beta_2^{\mathrm{I}}$ lines from the $K\beta_2^{\mathrm{II}}$ lines is also very hard for the same reason as in the case of Dy, and hence, these lines have been presented together in Fig. 4 (as $K\beta_2$ line). Whereas, ytterbium has a closed-shell electronic configuration, so for this case, it seems that the $K\beta_2^{\mathrm{II}}$ transitions should be distinguished from the $K\beta_2^{\mathrm{I}}$ line, but because of the possible open 4f shell, the two $K\beta_2$ lines combine again.

Summary and conclusions

The obtained theoretical results for the selected 4d-transition metals and 4f rare-earth elements may enable the low- and high-temperature diagnostics of the plasma parameters by the interpretation of K X-rays spectra emitted from the plasma, produced in different sources. Some of the presented results for ytterbium have been already used for obtaining the information about the plasma parameters (i.e., ionization level) generated by discharge pulsed power PFRP diode [7]. Moreover, in the future, these results for dysprosium can be useful in the interpretation of K X-ray spectra from the plasma produced by short-pulsed high power lasers irradiation in LULI, Palaiseau, France [16]. Our research for Mo will be also helpful for interpretation of K X-ray spectra from the plasma produced by X-ray generator Sandia Z-machine (Albuquerque, USA) [17]. The presented results may also be helpful for the interpretation of K X-ray spectra from the plasma generated by a plasma-focus device (e.g., PF-1000, Institute of Plasma Physics and Laser Microfusion, Warsaw, Poland), high-power lasers PHELIX in GSI (Darmstadt, Germany), PALS (Prague, Czech Republic), and potentially relevant to diagnostics of laser-produced plasmas as studied in connection with the researches of National Ignition Facility.

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