Theoretical simulation of the x-ray spectra of multiply ionized heavy atoms: The $K\alpha L^n$ spectra of molybdenum

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Multiconfiguration Dirac-Fock calculations in the average-level version with the inclusion of the transverse- (Breit) interaction, self-energy, and vacuum polarization corrections have been carried out on the $K\alpha L^n$ x-ray transitions of molybdenum in order to simulate its experimental ^{4}He- and ^{16}O-induced x-ray spectra. Lorentzian profiles convoluted with the Gaussian instrumental response have been assumed for the component lines. It has also been assumed that the spectrum is a linear combination of all the $K\alpha L^n$ lines and the coefficients of this combination have been chosen so as to obtain the best fit to experimental data. The ^{4}He-induced spectrum (without a significant contribution of the satellite lines) has been reproduced with excellent agreement, while in the case of the ^{16}O-induced spectrum the positions of the theoretical bands turned out to be shifted towards lower energies when compared with the experiment and their widths turned out to be smaller. These discrepancies are due to neglect of the effect of the M-shell holes, which results both in shifting of the bands' centers towards higher energies and in broadening of the bands. The latter can be overcome by assuming larger Gaussian linewidths. It has also been concluded that due to the complexity of the $K\alpha$ x-ray spectra in terms of the satellite lines, an analysis of the experimental $K\alpha L^n$ spectra without considering the theoretical studies on the structures of the $K\alpha L^n$ lines can lead to false interpretations.

I. INTRODUCTION

One of the salient features of heavy-ion-induced $K\alpha$ x-ray spectra is the high probability of multiple ionization of N, M, and L shells.[1] Generally, the shape of a $K\alpha$ x-ray spectrum depends both on the kind of inducing particles and the Z value of the element under study.

In the case of heavy elements the relativistic effects are essential in the interpretation of the spectra. The number of such relativistic calculations is however small. Recently extensive multiconfiguration Dirac-Fock (MCDF) and configuration-interaction (CI) studies including the transverse interaction and quantum electrodynamics (QED) corrections have been carried out on the satellite structure in the $K\beta$ x-ray spectrum of argon.[2]

In a previous paper,[3] hereafter referred to as I, relativistic MCDF calculations in the average-level (MCDF-AL) version with the inclusion of the transverse- (Breit) interaction, self-energy, and vacuum polarization corrections have been carried out on palladium to elucidate the structure of the $K\alpha L^n$ satellite lines in its x-ray spectra, which was the first systematic theoretical study on the structure of these lines for a heavy atom. It has been found[3] that for all the types of transitions (presented in I) the "average" relative positions of the groups of lines are close to the recently measured[4] experimental relative positions of appropriate $K\alpha L^n$ satellite lines while the best agreement is achieved for the transitions of the type $1s^{-1}2p^{-n}\rightarrow 2p^{-(n+1)}$.

As it has been concluded in I the results of detailed theoretical studies on the structure of $K\alpha L^n$ lines should be a good basis for the simulation of the various experimental spectra generated by different kinds of the inducing projectile.

Very recently Perny *et al.*[1] have performed high-resolution studies of the $K\alpha L^n$ satellite lines in ^{4}He- and ^{16}O-induced x-ray spectra of molybdenum. They have found that generating the spectrum by 28-MeV ^{4}He ions leads practically to principal lines, the satellite $K\alpha L^1$ lines being observed only as weak shoulders on the high-energy side of the principal lines.[1] On the contrary, acting with heavy 112-MeV ^{16}O ions results in strong $K\alpha L^n$ satellite lines,[1] because it is very likely that L-shell vacancies will appear apart from the K-shell vacancy.

The availability of their accurate data was the inspiration to perform a systematic study on the $K\alpha L^n$ transitions of molybdenum which would enable a simulation the experimental spectra. This can serve to illustrate how the knowledge of the structure of the particular $K\alpha L^n$ lines can be applied to sufficiently reproduce the experimental spectra. The present studies are based on the atomic multiconfigurational Dirac-Fock (MCDF) package developed by Grant and co-workers.[5,6]

II. THEORETICAL BACKGROUND

The computational method used in the present study has been described in detail in many papers.[2,5–9] Moreover, some basic ideas have been presented in I. However, for the sake of clarity, some essential details are very briefly recapitulated here.

Within the MCDF scheme the effective Hamiltonian for an N-electron system is to be expressed by

$$H=\sum_{i=1}^{N} h_D(i)+\sum_{\substack{i,j\\ i<j}}^{N} C_{ij} \ , \tag{1}$$

where $h_D(i)$ is the Dirac operator for ith electron (see paper I) and the terms C_{ij} account for electron-electron interactions and come from the one-photon exchange process. Each C_{ij} can be expressed[8] by

$$C_{ij}=1/r_{ij}+T(r_{ij}) , \tag{2}$$

where $1/r_{ij}$ is the Coulomb interaction operator (due to longitudinally polarized photons) and $T(r_{ij})$ is the transverse Briet operator (due to transversely polarized photons):

$$T(r_{ij})=-\frac{\boldsymbol{\alpha}_i\cdot\boldsymbol{\alpha}_j}{r_{ij}}+(\boldsymbol{\alpha}_i\cdot\boldsymbol{\nabla}_i)(\boldsymbol{\alpha}_j\cdot\boldsymbol{\nabla}_j)\frac{\cos(\omega r_{ij})-1}{\omega^2 r_{ij}} . \tag{3}$$

In the MCDF method an atomic state function (ASF) with the total angular momentum J and parity p is assumed in the multiconfigurational form:[2,5]

$$\Psi_s(J^p)=\sum_m c_m(s)\Phi(\gamma_m J^p) \tag{4}$$

where $\Phi(\gamma_m J^p)$ are configuration state functions (CSF), $c_m(s)$ are the configuration mixing coefficients for state s, and γ_m represents all information required to uniquely define a certain CSF.

Actually, in solving the eigenproblem for such a Hamiltonian the transverse (Breit) interaction (3) is neglected. The corresponding energy contribution is added as a first-order perturbation correction after self-consistency is achieved.[6]

In the standard MCDF-AL version of calculations[2,5] which has been applied in this work the energy functional is averaged over all the initial and final states and can be expressed by[5]

$$E=E_{\rm opt}+\sum_a \bar{q}_a\epsilon_a N(a,a)+\sum_{\substack{a,b\\ a\neq b}}\epsilon_{ab}N(a,b) , \tag{5}$$

where $\bar{q}_a$ is the generalized occupation number for orbital a, ϵ_a and ϵ_{ab} are the Lagrange multipliers, $N(a,b)$ is the overlap integral, and $E_{\rm opt}$ is taken in the form[2,5]

$$E_{\rm opt}=\frac{1}{n}\sum_{l=1}^{n} H_{ll} , \tag{6}$$

where n is the number of CSF's defining the initial and final states of the transitions considered, and H_{ll} are the diagonal contributions to the Hamiltonian matrix.

In this version of calculations the orbitals are to be determined only in the first step. In the second step the coefficients $c_m(s)$ corresponding to the orbitals found in the first step are determined by diagonalizing the matrix of the Hamiltonian in the space of the CSF's. Because the orbitals are common for all the initial and final states, applying MCDF-Al version is especially convenient for performing calculations of the probabilities of transitions between the states under consideration. It is evident that for each particular state such orbitals yield higher energy than those obtained from optimal-level versions of MCDF[2,5] (MCDF-OL) calculations (the effect of relaxation). However, usually all energy levels are shifted by approximately the same extent (see Ref. 3).

Apart from the transverse- (Breit) interaction two types of energy corrections are included, namely the self-energy and vacuum polarization corrections (see Refs. 3 and 6). The formulas for the transition-matrix elements, spontaneous emission probabilities, and oscillator strengths can be found in the work of Grant.[9]

III. RESULTS AND DISCUSSION

The structures of palladium energy levels and the structures of the components of its x-ray spectra corresponding to the particular transition types of the $K\alpha L^n$ lines have been described in detail in I. Because the case of molybdenum is qualitatively the same as the case of palladium, the transition diagrams are not presented here.

All possible CSF's in j-j coupling scheme due to the nonrelativistic configurations listed in Table I were used in the calculations. The full lists of j-j CSF's are recorded in the transition diagrams presented in I.

A detailed analysis of all the transitions for the $K\alpha L^n$ lines ($n=0,1,2,3$) has been carried out as in I. The only difference is that, contrary to the previous work, in the stick spectra the statistical populations of the initial states have been taken into account; these are proportional to $2J+1$, J being the total angular momentum of a

TABLE I. CSF sets used in the calculations of the structures of the particular transition types of the $K\alpha L^n$ lines. The numbers of CSF's in j-j coupling scheme are given in parentheses.

Transition type	CSF sets Initial	Final
$K\alpha L^0$	$1s^1 2s^2 2p^6$ (1)	$1s^2 2s^2 2p^5$ (2)
$K\alpha L^1$		
$(1s2s)^{-1}\rightarrow(2s2p)^{-1}$	$1s^1 2s^1 2p^6$ (2)	$1s^2 2s^1 2p^5$ (4)
$(1s2p)^{-1}\rightarrow 2p^{-2}$	$1s^1 2s^2 2p^5$ (4)	$1s^2 2s^2 2p^4$ (5)
$K\alpha L^2$		
$1s^{-1}2s^{-2}\rightarrow 2s^{-2}2p^{-1}$	$1s^1 2s^0 2p^6$ (1)	$1s^2 2s^0 2p^5$ (2)
$(1s2s2p)^{-1}\rightarrow 2s^{-1}2p^{-2}$	$1s^1 2s^1 2p^5$ (7)	$1s^2 2s^1 2p^4$ (8)
$1s^{-1}2p^{-1}\rightarrow 2p^{-3}$	$1s^1 2s^2 2p^4$ (8)	$1s^2 2s^2 2p^3$ (5)
$K\alpha L^3$		
$1s^{-1}2s^{-2}2p^{-1}\rightarrow(2s2p)^{-2}$	$1s^1 2s^0 2p^5$ (4)	$1s^2 2s^0 2p^4$ (5)
$1s^{-1}2s^{-1}2p^{-2}\rightarrow 2s^{-1}2p^{-3}$	$1s^1 2s^1 2p^4$ (16)	$1s^2 2s^1 2p^3$ (10)
$1s^{-1}2p^{-3}\rightarrow 2p^{-4}$	$1s^1 2s^2 2p^3$ (10)	$1s^2 2s^2 2p^2$ (5)

state. Moreover, to analyze the shapes of the particular components of the spectrum for all transition types of each $K\alpha L^n$ satellite two theoretical spectra have been constructed: one being a sum of the Lorentzian natural line shapes with a width of 6.82 eV (Ref. 10) (dotted lines), and for better comparison with experimental spectra, the other one being a convolution of the sum of the Lorentzian line shapes with the Gaussian instrumental response (solid lines).

For each $K\alpha L^n$ satellite is also given the summary spectrum constructed under the assumption that the populations of $2s$ and $2p$ holes depend only on the number of ways in which a particular initial-hole state can be formed (the influence of the Coster-Kronig transitions has also been neglected).

The subsequent type of $K\alpha L^n$ satellites are considered in Figs. 1–3. It can be noted that the convolution of the sum of Lorentzian line shapes with the Gaussian instrumental response greatly smoothes the resultant spectrum.

When analyzing the shapes of the particular components to the spectrum it can be first observed that the most scattered and structured bands are in the case of transitions from the initial states having one $2s$ hole. In other cases (except for the transitions of the $K\alpha L^0$ and those from the initial states having only a whole $2s$ subshell removed) the components are usually grouped to give two little structured bands. It must be borne in mind at this point that in resolving the experimental spectra the contribution of a particular $K\alpha L^n$ band to the spectrum is approximated by two Voigt profiles (convolution of a single Lorentzian line shape with the Gaussian instrumental response), one for $K\alpha_1 L^n$ band and one for $K\alpha_2 L^n$ band. From Figs. 1–3, however, it results that although in each case we can distinguish two "bands" of remarkably high intensity in the spectrum, just because of their complexity none of them can be represented as a single Voigt function, even in a very crude approximation.

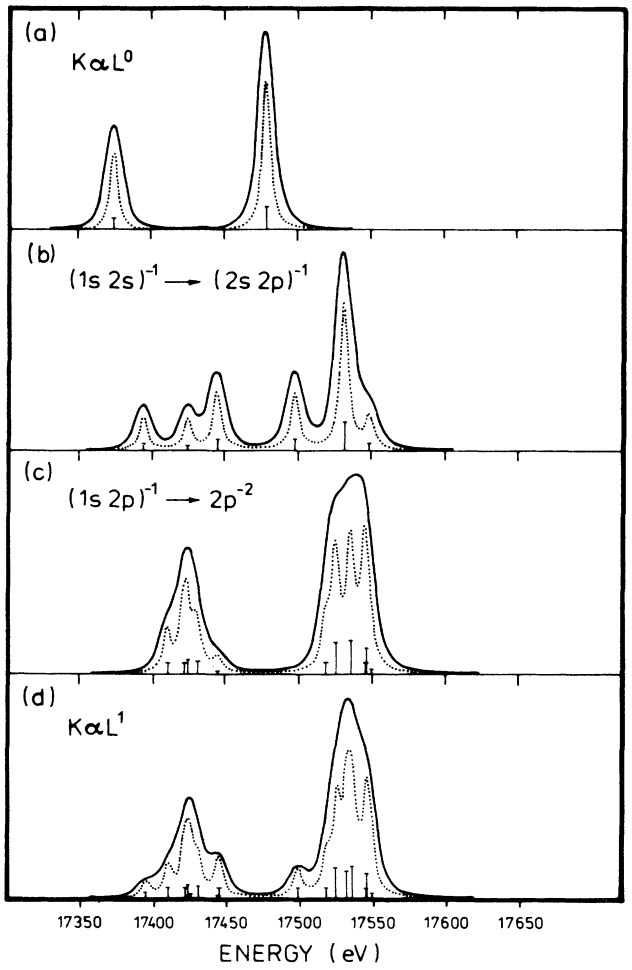

FIG. 1. Calculated stick (line positions with their intensities, relative to the same scale) and synthesized spectra [a sum of the Lorentzian line shapes with a width of 6.82 eV, (Ref. 10) dotted lines, and a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having a width of 10.5 eV, solid lines] for $K\alpha L^n$ transitions of the types: (a) $K\alpha L^0$ (principal lines), (b) $K\alpha L^1$ in the case of $(1s2s)^{-1} \rightarrow (2s2p)^{-1}$, (c) $K\alpha L^1$ in the case of $(1s2p)^{-1} \rightarrow 2p^{-2}$, and (d) $K\alpha L^1$, summary spectrum [(b)+(c)].

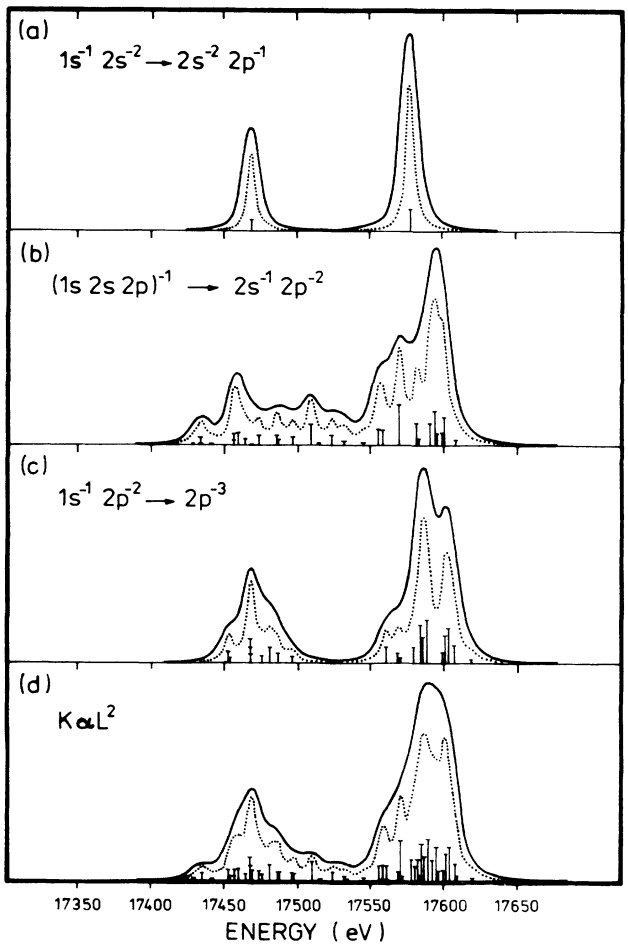

FIG. 2. Same as Fig. 1, but for $K\alpha L^2$ satellite transitions of the following types: (a) $1s^{-1}2s^{-2} \rightarrow 2s^{-2}2p^{-1}$, (b) $(1s2s2p)^{-1} \rightarrow 2s^{-1}2p^{-2}$, (c) $1s^{-1}2p^{-2} \rightarrow 2p^{-3}$, and (d) $K\alpha L^2$, summary spectrum [(a)+(b)+(c)].

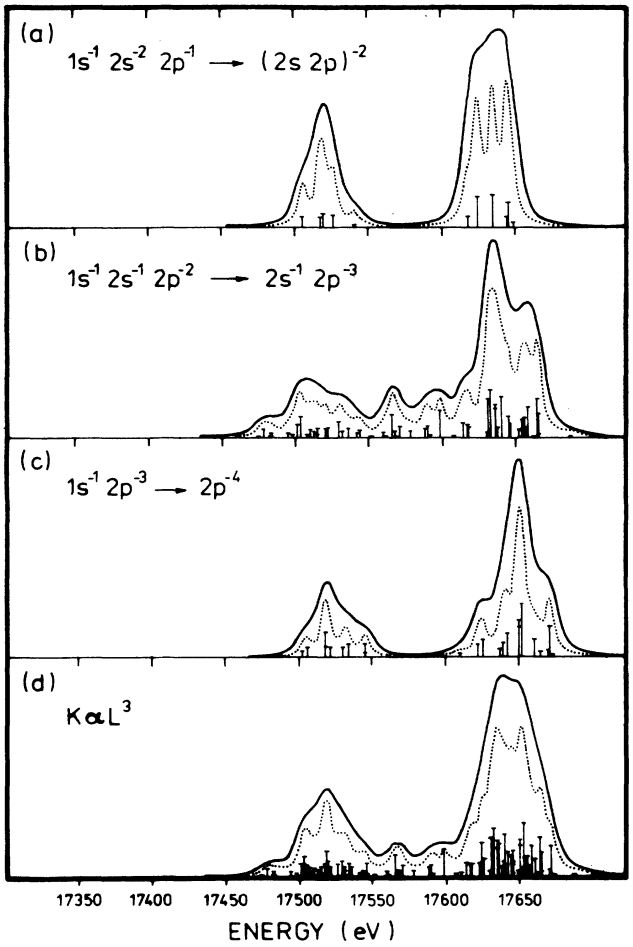

FIG. 3. Same as Fig. 1, but for $K\alpha L^3$ satellite transitions of the following types: (a) $1s^{-2}2s^{-2}2p^{-1} \rightarrow (2s2p)^{-2}$, (b) $1s^{-1}2s^{-1}2p^{-2} \rightarrow 2s^{-1}2p^{-3}$, (c) $1s^{-1}2p^{-3} \rightarrow 2p^{-4}$, and (d) $K\alpha L^3$, summary spectrum [(a)+(b)+(c)].

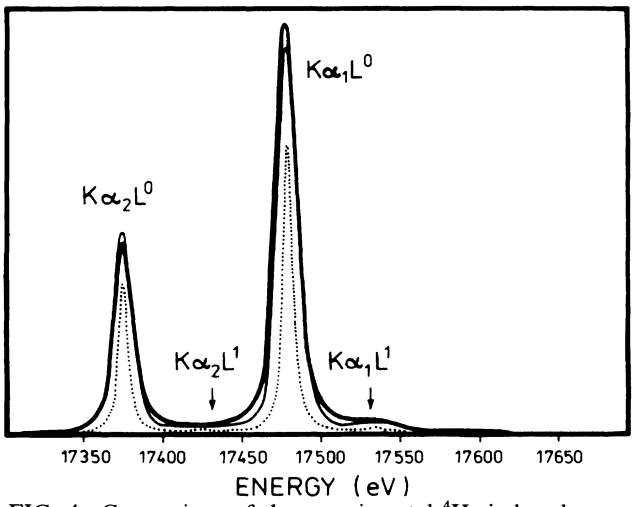

FIG. 4. Comparison of the experimental ^{4}He-induced x-ray spectrum of molybdenum (thick line) with the synthesized theoretical spectra: a sum of the Lorentzian line shapes with a width of 6.82 eV (Ref. 10) (dotted line) and a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having a width of 10.5 eV (solid line).

As it has been mentioned in the Introduction the shape of an x-ray spectrum of a given atom depends on the type of inducing particle. Obviously, each spectrum is a linear combination of the components corresponding to the particular transitions, the coefficients of this combination being proportional to the relative intensities of the bands. The change in kind of the inducing particle changes the coefficients of this combination which is reflected in the shape of the spectrum. Actually it can be assumed with high probability that the contributions of the particular transitions within a given $K\alpha L^n$ satellite are not remarkably dependent on the inducing particles. Therefore an

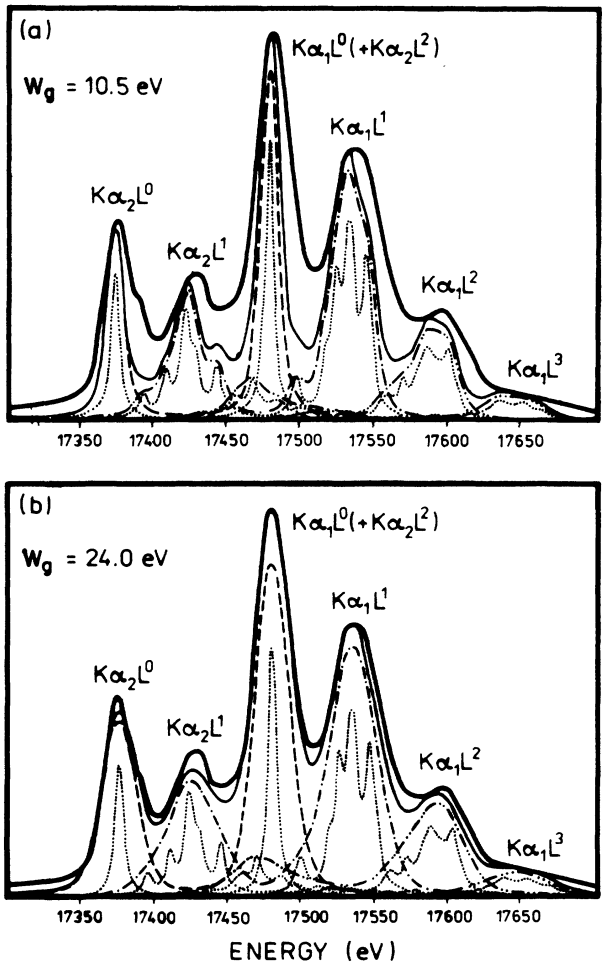

FIG. 5. Comparison of the experimental ^{16}O-induced x-ray spectrum of molybdenum (thick line) with the two different theoretically simulated spectra (solid lines) constructed as sums of the bands resulting from the transitions of $K\alpha L^n$ type (see text). Both figures also show the contributions of the particular $K\alpha L^n$ bands to theoretical spectra being a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having a width of 10.5 eV (a) and 24.0 eV (b) (dashed lines: $K\alpha L^0$, — — —; $K\alpha L^1$, —·—·—·; $K\alpha L^2$, —···—; $K\alpha L^3$, —···—). Moreover, for comparison, the figures show the theoretical spectra for each $K\alpha L^n$ band being only a sum of the Lorentzian line shapes with a width of 6.82 eV (Ref. 10) (dotted lines). W_g is the Gaussian width at half maximum.

x-ray spectrum can approximately be expressed as a linear combination of the summary bands, each of them corresponding to a different $K\alpha L^n$ satellite type. Unfortunately, it is practically impossible to theoretically calculate the respective linear combination coefficients. However, given the experimental spectrum we can evaluate these coefficients so as to best fit the spectrum constructed to the experimental one.

In Fig. 4 are presented the theoretically simulated spectra of ^{4}He-induced molybdenum, together with the experimental spectrum of Perny *et al.*[1] As it is shown, the dominant contribution comes from $K\alpha L^0$ transition type. It can also be observed that both the shape of the experimental spectrum and the positions of the band centers are reproduced with an excellent accuracy by the convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response having a width of 10.5 eV (solid line).

The case of ^{16}O-induced x-ray spectrum of molybdenum is presented in Figs. 5(a) and 5(b). Both simulated spectra have been constructed as sums of the $K\alpha L^n$ bands obtained by the convolution of the sum of the Lorentzian natural lines shapes with two different Gaussian instrumental responses (solid lines). The theoretical spectrum in Fig. 5(a) has been obtained having assumed the Gaussian linewidth of 10.5 eV which is exactly the instrumental response.[1] It can be seen that although the shape is generally consistent with the experimental one,[1] the bands are evidently too narrow, and the $K\alpha_2 L^1$ band has too many details not observed experimentally. It can also be noted that all the theoretical bands are shifted to the left when compared with the experiment, by about 5 eV for $K\alpha L^0$ lines and 10–15 eV for $K\alpha L^n$ satellites. As it has been pointed out by Perny *et al.*[1] and Polasik,[3] such discrepancies can be attributed to the M-shell vacancies which are not considered in the present simulation. Those vacancies result in both a shifting of the transition energies towards higher values and the production of broader and smoother bands. The two latter effects are due to the fact that many transitions emerge whose energies are very close.

To reflect the effect of broadening a simulation has been performed with the Gaussian width of 24 eV. The theoretical and experimental spectra are compared in Fig. 5(b). For a better compairson, the effect of shifting the transition energies due to M-shell holes has been taken into account by shifting the theoretical spectrum by 5 eV to the right. As it can be observed the agreement with the experiment is now satisfactory.

In Figs. 5(a) and 5(b) have also been shown the particular $K\alpha L^n$ bands as components of the theoretically simulated spectra (being a convolution of the sum of the Lorentzian natural line shapes with the Gaussian instrumental response) and, for comparison, the theoretical spectra for each $K\alpha L^n$ band being only a sum of the Lorentzian natural line shapes (dotted lines). It can easily be seen that the contributions of the particular $K\alpha L^n$ bands strongly overlap. Thus, e.g., the $K\alpha_2 L^2$ band is fully covered by a strong $K\alpha_1 L^0$ principal band and $K\alpha_2 L^3$ by a strong $K\alpha_1 L^1$ band. Moreover, as it has been noted above, the theoretical shape of each $K\alpha L^n$ satellite band obtained with ordinary linewidths of the Gaussian instrumental response [Fig. 5(a)] has too many details and cannot be well represented as a single Voigt function. However, the consideration of the effect of M-shell holes by assuming greater Gaussian linewidths makes those details vanish, and the resultant bands are now closer to some broader Voigt profiles.

A comparison of two last simulations shows the importance of the effect of M-shell holes on the $K\alpha L^n$ x-ray spectra. Obviously, in the present work this effect has been only very crudely taken into account by shifting the spectrum and broadening the lines. Unfortunately, there is no such simple way to simulate the effect of the asymmetry of the $K\alpha_2 L^0$ band. This confirms the conclusion from I that to accurately reproduce both the positions of the satellites and the shape of the experimental $K\alpha L^n$ x-ray spectrum it is necessary to include in the calculations the states having holes in the M shell.

The values of the relative intensities of the bands resulting from the theoretical simulation performed with the Gaussian width of 24 eV are collected in Table II. In this table are also given the relative intensities of the satellite lines in ^{16}O-induced x-ray spectrum of molybde-

TABLE II. Comparison of the values of the relative intensities of the $K\alpha L^n$ bands in the ^{16}O-induced x-ray spectrum of molybdenum resulting from the theoretical simulation with the corresponding values obtained by decomposition of the spectrum into the Voigt profiles [from the work of Perny *et al.* (Ref. 1)].

Type of $K\alpha L^n$ band	Theoretical simulation $I(K\alpha_i L^n)$	Theoretical simulation $\frac{I(K\alpha_2 L^n)}{I(K\alpha_1 L^n)}$	Decomposition into the Voigt profiles $I(K\alpha_i L^n)$	Decomposition into the Voigt profiles $\frac{I(K\alpha_2 L^n)}{I(K\alpha_1 L^n)}$
$K\alpha_1 L^0$	100.0	0.525	100(1)	0.400
$K\alpha_2 L^0$	52.5		40(4)	
$K\alpha_1 L^1$	100.1	0.485	102(10)	0.392
$K\alpha_2 L^1$	48.5		40(4)	
$K\alpha_1 L^2$	44.0	0.466	29(3)	0.379
$K\alpha_2 L^2$	20.5		11(2)	
$K\alpha_1 L^3$	8.4	0.429	0.8(0.3)	
$K\alpha_2 L^3$	3.6			

num obtained by Perny *et al.*[1] by decomposition of the spectrum into the Voigt profiles. As it is shown, they are very far from the values resulting from the theoretical simulation. This indicates that the complexity of $K\alpha L^n$ x-ray spectra of multiply-ionized heavy atoms clearly prohibits their decomposition on the basis of the experimental data only, and the theoretical knowledge is necessary to perform this correctly.

IV. CONCLUSIONS

The present study on theoretical simulation of the $K\alpha L^n$ x-ray spectra of molybdenum has shown that the model in which a spectrum is represented as a sum of the bands resulting from transitions of $K\alpha L^n$ type can satisfactorily reproduce the experimental spectra of heavy atoms including the satellite lines. It has also been shown that in the case of ^{16}O-induced x-ray spectrum the effect of the M-shell holes is not negligible and must be taken into account at least by shifting the spectrum towards higher energies and broadening the bands. However, to accurately reproduce both the positions of the lines and the shape of the experimental spectrum including $K\alpha L^n$ satellites it is necessary to perform a detailed investigation in which various M-shell holes will be taken into account together with L-shell holes (the $K\alpha L^n M^r$ lines). The work on this problem is already in progress, and the results will be published in forthcoming papers.

Another important conclusion is that due to the complexity of $K\alpha L^n$ x-ray spectra of multiply-ionized heavy atoms analysis by decomposition of the spectrum into the Voigt profiles can lead to false interpretations and that the detailed theoretical knowledge of the structure of the $K\alpha L^n$ satellite lines is necessary to analyze the experimental spectra correctly. Because, for example, the relative intensities of the satellite lines are very important parameters which are used in the calculations of the primary vacancies distribution,[11] and in the nuclear fusion reaction studies[12] it is evident that they must be estimated as accurately as possible. This is a strong argument for the necessity of the theoretical studies on the x-ray spectra.

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