Correlation effects in the $M_{4,5}N_{4,5}O$ Auger spectra of Xe

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The $M_{4,5}N_{4,5}O$ Auger spectra of Xe have been measured and compared with theoretical profiles. Single-particle predictions are found to deviate strongly from experiment in the case of the $M_{4,5}N_{4,5}O_1$ transitions. Multiconfiguration calculations which take into account the mixing between the $4d^9 5s^1 5p^6$ and $4d^9 5s^2 5p^4 5d^1$ configurations reproduce the observed structure reasonably well.

I. INTRODUCTION

The $M_{4,5}N_{4,5}O$ Auger spectra of Xe had been presented some time ago together with the $M_{4,5}NN$ Auger spectra.[1] The single-configuration prediction was found to be satisfactory in the case of the $M_{4,5}N_{4,5}O_{2,3}$ transitions. The experimental spectrum of the $M_{4,5}N_{4,5}O_1$ transitions, however, contained a strong satellite structure which was not reproducible by the single-configuration calculations.

The satellite structure associated with ionization in the outer $5s$ shell of Xe has been the object of many recent studies.[2-6] These satellite lines are caused by the process in which the $5s$ hole is filled by a $5p$ electron with simultaneous excitation of another $5p$ electron to a $5d$ or $6s$ state. The process, for example, produces the satellites in the $5s$ photoelectron and $N_{4,5}OO$ Auger electron spectrum of Xe observed and analyzed recently.[2-6] The same process also takes place in the $4d^{-1}5s^{-1}$ final state of the $M_{4,5}N_{4,5}O_1$ Auger transitions giving rise to a strong low-kinetic-energy satellite structure. The failure of the single-particle picture in describing the observed structure is thus explainable. Multiconfiguration calculations were found to be successful in reproducing the $M_{4,5}OO$ spectrum of Xe. The same kind of calculations are therefore performed in this work in view to analyze the $M_{4,5}N_{4,5}O_1$ spectrum of Xe in detail.

Previous studies show a strong increase in the intensity of these correlation satellites in going from the single-hole state $5s^{-1}$ to the double-hole state $5s^{-1}5p^{-1}$. This clearly indicates that the correlation effects are very sensitive to the degree of the ionization and the states of the other electrons in an atom. In the present case we have a deep $4d$ hole accompanying the $5s$ hole. It is thus very interesting to study the strength of the process in this particular case. The investigations are carried out by comparing the experiment with the previous results as well as with the multiconfiguration calculations.

II. EXPERIMENTAL

A high-resolution experimental study of the $M_{4,5}N_{4,5}O$ Auger spectrum of xenon was carried out by means of a cylindrical-mirror spectrometer at the University of Oulu. The observed Auger electrons were excited with the use of a 3-keV electron beam.[7] The $M_{4,5}N_{4,5}N_{4,5}$ Auger spectrum of xenon was measured simultaneously with the $M_{4,5}N_{4,5}O$ spectrum. The absolute energies given in Refs. 1 and 8 were slightly corrected to correspond the new energy values 203.499 and 804.458 eV for the Ar $L_3M_{2,3}M_{2,3}(^1D_2)$ and Ne $KL_{2,3}L_{2,3}(^1D_2)$ calibration lines, respectively.[9]

The overall shape of the $M_{4,5}N_{4,5}O$ Auger spectrum depicted in Fig. 1(d) is very similar to that shown in Ref. 1. Higher resolution and better statistics are, however, characteristics of the present spectrum compared to the study of Ref. 1.

III. RESULTS AND DISCUSSION

Previous investigations indicated that the single-particle predictions may not suffice in reproducing the measured structure of the $M_{4,5}N_{4,5}O$ spectra.[1] The results of the higher-resolution study showed further discrepancies with the existing calculated spectra.[1] This motivated more accurate calculations of the transitions.

Single-configuration calculations were first carried out for the $3d^{-1}\rightarrow 4d^{-1}5s^{-1}$ and $3d^{-1}\rightarrow 4d^{-1}5p^{-1}$ transitions. The energies of the transitions were determined by taking the difference of the energies obtained by performing separate relativistic self-consistent-field (SCF) calculations for the initial single-hole and final double-hole state with the use of the multiconfiguration Dirac-Fock (MCDF) computer code of Grant *et al.*[10] (called the ΔSCF method). The transition probabilities were obtained with the aid of the matrix elements of the Coulomb interaction between the initial and final states, where the final state also contains the continuum electron wave function. The radial integrals of the Coulomb interaction were taken from the tables of McGuire.[11] At higher Auger energies the tabulated radial integrals of McGuire are found to reproduce the observed intensity distributions between the fine-structure components reasonably well. This indicates that the relative intensities of the lines are not too sensitive to the computation method of the radial integrals. The calculated intensities for the low-energy transitions of NOO type may, however, depend more on the calculation method of the integrals.

By comparing the single-configuration profile shown in Fig. 1(a) with the experimental spectrum [Fig. 1(d)], a clear disagreement can be found in the case of the intensi-

ty distribution of the $M_{4,5}N_{4,5}O_1$ transitions. Calculations for the $M_{4,5}N_{4,5}O_{2,3}$ transitions seem to agree better with experiment, although the calculated and experimental absolute energies disagree slightly.

Next the correlation effects in the $4d^95s^15p^6$ final state of the $M_{4,5}N_{4,5}O_1$ decay were studied. Final-state wave functions were obtained as linear combinations of the wave functions of the correlating $4d^95s^15p^6$ and $4d^95s^25p^45d^1$ states.

Several energy calculations were performed in the final state in order to test the sensitivity of the mixing to the choice of the optimization method and the basis set. Some results for the transitions to the $J=2$ levels are depicted in Fig. 2. Also, the single-configuration profile is shown in Fig. 2(a) for comparison. Figure 2(b) displays an optimal level (OL) calculation, where the wave functions and mixing coefficients for the lowest-energy level of the $4d^95s^15p^6$ configuration were optimized and the basis set was made of six relativistic configurations. Extra peaks appear at the low-energy side of the main lines. Their energy separation from the main peaks and intensity slightly vary in going on the basis set of fifteen configurations with the OL optimization method [Fig. 2(c)]. Using the average-level (AL) optimization approach of Grant's computer code, the intensity of the satellites increases as can be seen by comparing Figs. 2(c) and 2(d). The results for the energy levels with $J=1$ and 3 behave analogously with the results of Fig. 2.

The profile of Fig. 2(d) is used together with the corresponding profiles for the $J=1$ and 3 levels to obtain the multiconfiguration picture for the $M_{4,5}N_{4,5}O_1$ transitions in Fig. 1(b). The $M_{4,5}N_{4,5}O_{2,3}$ profile of Fig. 1(b) is from the single-configuration calculation. In passing from the single-configuration to the multiconfiguration description for the $M_{4,5}N_{4,5}O_1$ transitions [Fig. 1(a) to 1(b)] we clearly see that the correlation leads to an energy shift and a redistribution of the intensity between the main (around 570 to 573 eV in the M_5 group) and satellite ($\sim$567 eV) lines in a good agreement with experiment. Energy difference between the main lines and satellites is, however, slightly underestimated by theory. The difference is very sensitive to the computation approach, as can be seen from Fig. 2.

The $5d$ orbital collapse takes place in going from neu-

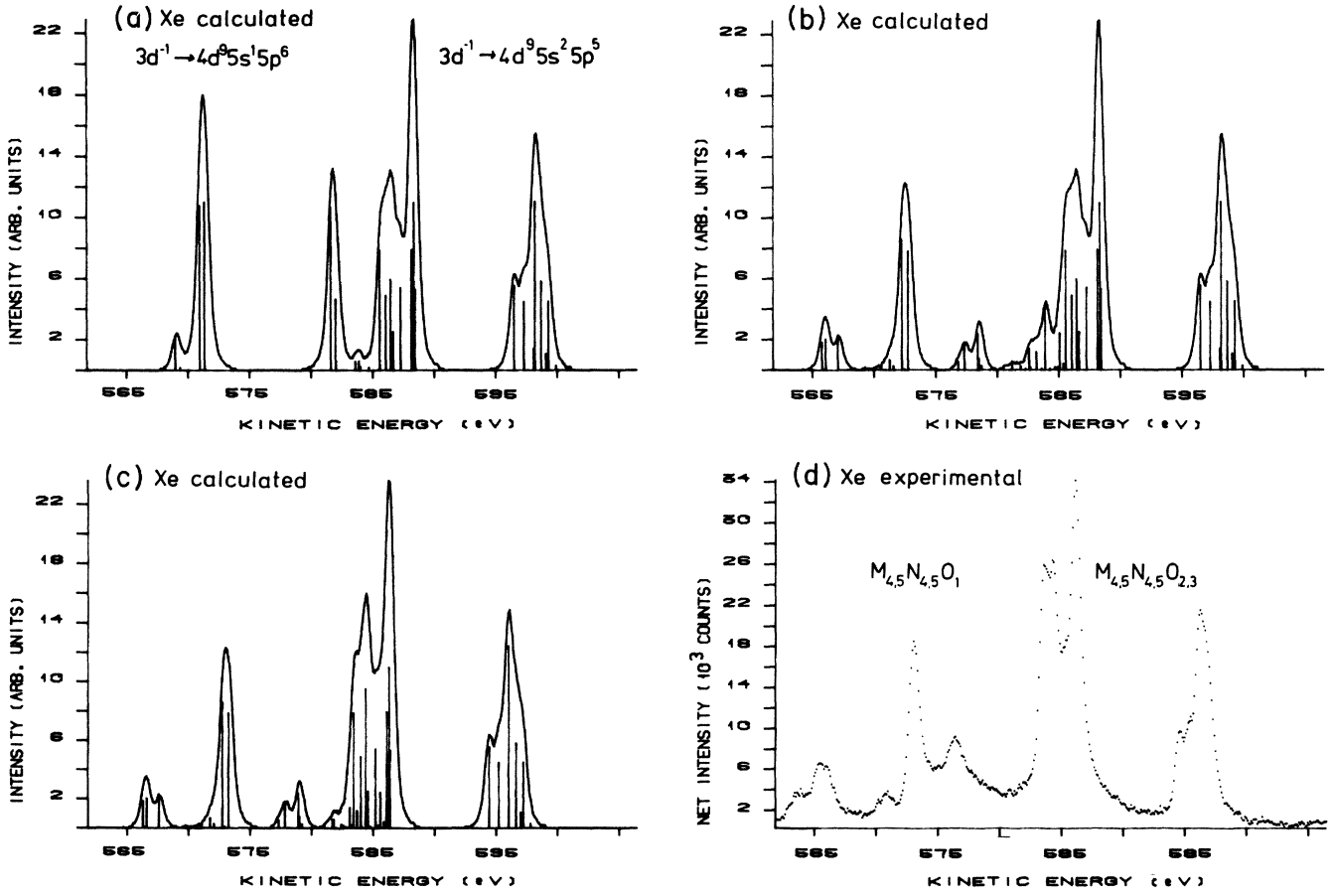

FIG. 1. (a) Single-configuration profile for the $M_{4,5}N_{2,3}O$ Auger transitions of Xe. (b) Calculated spectrum with the multiconfiguration description for the $M_{4,5}N_{2,3}O_1$ and the single-configuration description for the $M_{4,5}N_{2,3}O_{2,3}$ transitions. (c) Calculated spectrum from (b) where the $M_{4,5}N_{2,3}O_{2,3}$ spectrum is shifted by 2.1 eV to lower kinetic energies and the $M_{4,5}N_{4,5}O_1$ spectrum by 0.5 eV to higher energies. (d) Experimental $M_{4,5}N_{2,3}O$ Auger spectrum of Xe.

tral to ionized states of Xe. The $5d$ orbital does not overlap much with the $5s$ and $5p$ orbitals in the neutral atom. In passing to the ionized states of Xe, the interaction $5s^15p^6 \leftrightarrow 5s^25p^45d^1$ becomes very strong due to the $5d$-wave-function collapse. The mixing of the configurations is very sensitive to their energy difference, the estimates for which easily vary depending on the computation method. Hansen has pointed out the importance to include the higher members of the $5s^25p^4md^1$ Rydberg series as well as the continuum d states in the case of the single-$5s$-hole state.[12] In the present double-hole state we have found a reasonably good agreement with experiment with the use of the limited basis set, which considerably simplifies the calculations. Further extension of the basis set from those depicted in Fig. 2 to cover all the relativistic configurations which result from the $4d^95s^15p^6$ nonrelativistic one, tends to lead to the overestimation of the satellite intensity. The OL optimization approach, however, partly compensates for the improper increase of the satellite intensity [compare Figs. 2(b) and 2(c)]. No effort to include higher members of the bound d series has been done in this work, because of a drastic increase in the computation time. A satisfactory description is, however, attained by limiting the basis set to not over fifteen relativistic configurations for $J=2$ (Fig. 2), for example. This can be considered as a good compromise, because the computations with a full basis set are beyond our computer resources.

The same kind of correlation structure was observed in the $5s$ photoelectron and $NO_1O_{2,3}$ Auger electron spectra. Comparison between the present result and the findings obtained recently for the $5s^15p^5$ final state of the NOO transitions[6] shows that the intensity ratio between the main and satellite lines is considerably smaller in the present case. Owing to different kind of fine structures in both spectra, the comparison is complicated. It, however, indicates the high sensitivity of the electron correlation accompanying the $5s$-hole state to the states of the surrounding electrons. The collapse of the $5d$ orbital and its overlap with the $5s$ and $5p$ orbitals is highly sensitive to the strength of the interelectronic repulsion. This, furthermore, is affected by the degree and depth of the ionization.

So far only the $4d^95s^15p^6 \leftrightarrow 4d^95s^25p^45d^1$ correlation

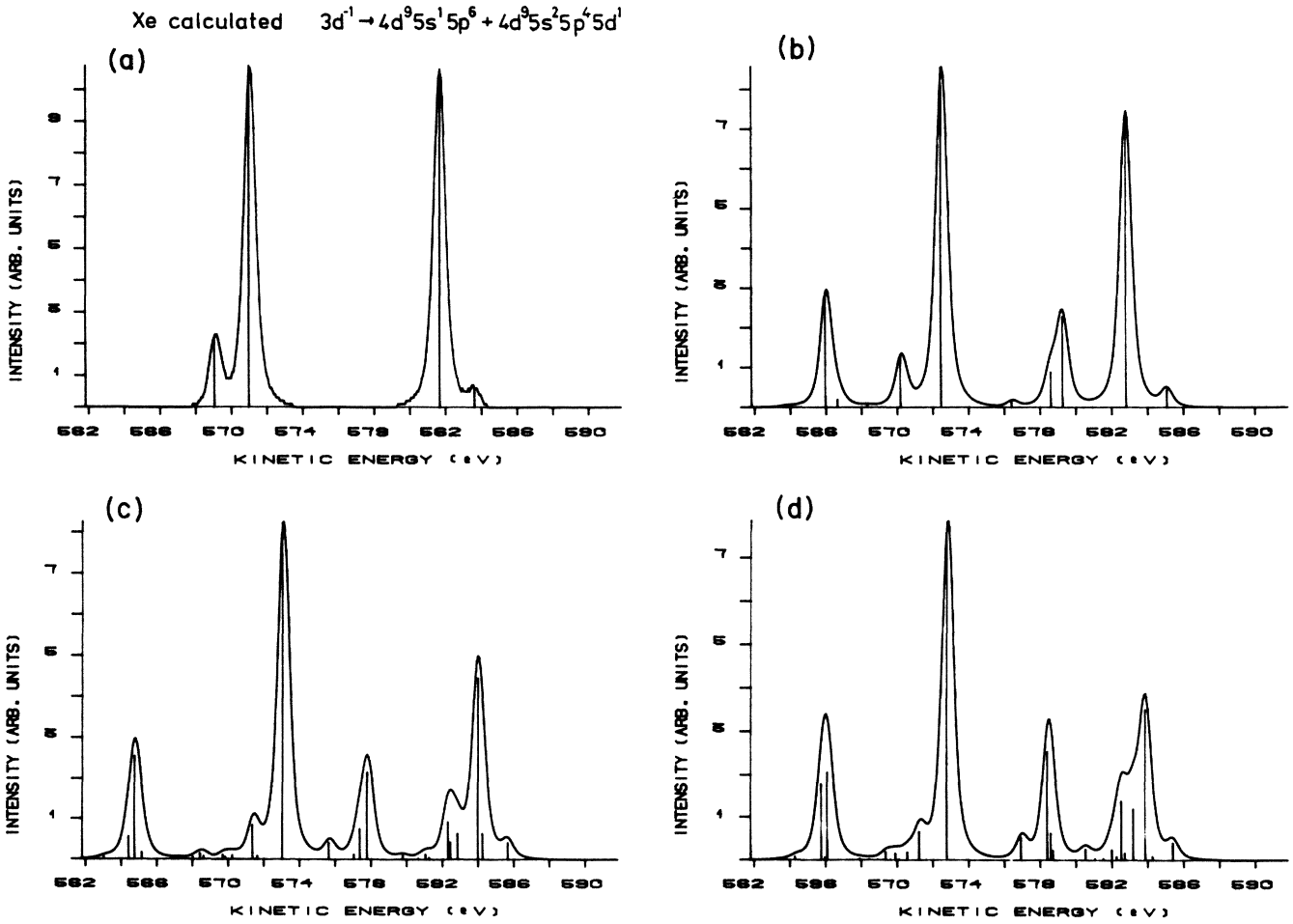

FIG. 2. Influence of the basis set and the optimization method to the correlation effects in the $4d^95s^15p^5$, $J=2$ final states of the $M_{4,5}N_{4,5}O_1$ Auger decay of Xe. (a) Single-configuration calculation. (b) Multiconfiguration OL calculation with six $J=2$ final-state configurations. (c) Multiconfiguration OL calculation with fifteen $J=2$ final-state configurations. (d) AL calculation with the same basis set as in (c).

has been considered. When this main contribution has been taken into account, the calculated profile seems to reproduce the experiment fairly well. The two transitions, $M_{4,5}N_{4,5}O_1$ and $M_{4,5}N_{4,5}O_{2,3}$, however, clearly lie too far from each other energetically. This is nicely demonstrated in Fig. 1(c), where we have shifted the $M_{4,5}N_{4,5}O_{2,3}$ transitions by 2.1 eV to lower energies and the $M_{4,5}N_{4,5}O_1$ transitions by 0.5 eV to higher energies arriving at a much better overall agreement with experiment.

In order to study the energy shifts more carefully, we have compared the calculated single-configuration profile of the $3d^{-1}\rightarrow 4d^{-2}$ transitions with experiment in Fig. 3. Experimental and calculated energies seem to agree within 1.8 eV. ΔSCF calculations were found to agree within 0.2 eV for the $3d$ binding energy and within 2.0 eV for the double $4d$-hole-state binding energy. Thus an energy shift of 1.0 eV per one hole in the $4d$ shell remains. This is in agreement with the experimental and calculated $4d$ binding-energy difference. Thus the correlation contribution to the binding energy of the double-hole state equals the sum of the correlation contributions to the binding energies of the single-hole states.[13]

Calculated and experimental Auger energies of the $3d^{-1}\rightarrow 4d^{-1}5p^{-1}$ transitions do not agree as well as those of the $3d^{-1}\rightarrow 4d^{-2}$ transitions. This indicates larger energy shift for a hole state where one $5p$ electron is missing. From the $5p^{-2}$ final state of the $N_{4,5}O_{2,3}O_{2,3}$ Auger transitions we obtain an energy shift of 0.8 eV per hole, in good agreement with the energy difference from experimental and calculated $5p$ binding energies. The simple sum rule for the correlation contributions no longer holds for the $M_{4,5}N_{4,5}O_{2,3}$ transitions, which show a shift of 2.1 eV, whereas a value of 1.6 eV is estimated using the sum rule. The sum rule fails to agree for the $M_{4,5}N_{4,5}O_1$ transitions, too, due to the larger correlation shift for the $5s^{-1}$ state accompanied by a $4d$ hole than for a single $5s$-hole state.

The experimental spectrum in Fig. 1(d) contains some extra structure, which is not reproduced by the calculations [Fig. 1(c)]. A satellite structure due to the shake-up process accompanying the initial ionization should appear on the low-energy side of the main lines. The MCDF calculations predict that the $5p\rightarrow 6p$ shake-up satellites lie 1–8 eV lower in energy than the main lines. Due to the coupling between the $6p$ electron and the core holes, shake-up satellites show a very rich fine structure. The shake-up satellites from the $M_{4,5}N_{4,5}O_{2,3}$ groups fall on the same energy region with the correlation satellites from the $M_{4,5}N_{4,5}O_1$ groups, furthermore, complicating the analysis of the spectrum. States due to the excitations of $5p\rightarrow 6p$ type, do not correlate strongly with the ground state, whereas the double excitations may allow mixing, which may result in an energy shift now observed for the final state with a $5p$ hole.

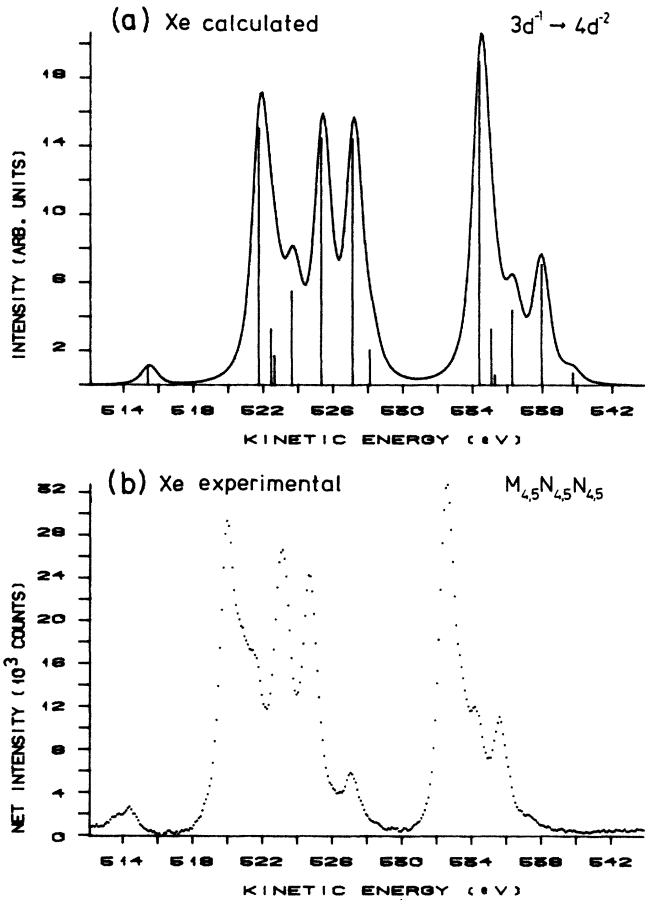

FIG. 3. Calculated and experimental $M_{4,5}N_{4,5}N_{4,5}$ Auger spectra of Xe.

The high-energy electron beam used can ionize the deeper M and N levels. Via the Auger decay, this may lead to doubly ionized states, where one of the holes is created in the $3d$ level. The satellite transitions, when these double-hole states decay to the triple-hole states, fall energetically on the low-energy side of the normal Auger transitions. Thus the satellites associated with the $M_{4,5}N_{4,5}O_{2,3}$ transitions overlap with the $M_{4,5}N_{4,5}O_1$ transitions also complicating their analysis in more detail. The foretold effect due to the mixing of the $4d^9 5s^1 5p^6$ and $4d^9 5s^2 5p^4 5d^1$ final states, however, seems to give the strongest contribution to the observed satellite structure. More detailed calculations which take into account all the correlation effects are needed to fully understand the spectrum.

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