Simultaneous determination of radiative and nonradiative decay channels in the neon *K* shell

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The photoelectron-photoion coincidence method is shown to be very successful for the quantitative investigation of the ratio of radiative to nonradiative transitions and for the ratio of single to double Auger transitions. These decay probabilities are important parameters for analytical methods as well as for theoretical descriptions. The method is demonstrated for the neon 1*s* decay. Especially the fluorescence yield and the yield for the double Auger process have been determined both experimentally and theoretically.

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The decay of inner-shell hole states takes place by radiative and nonradiative transitions where the filling of the vacancy by an outer-shell electron is accompanied by the emission of a photon or of Auger electrons (one electron for single Auger, two electrons for double Auger transitions, etc.). In the sub-keV region of transition energies, the single Auger emission is by far the dominant decay process and radiative or double Auger transitions usually are neglected. The ratios of radiative to nonradiative transitions and the ratio of single to double Auger transitions, however, are important quantities for experimental as well as for theoretical studies. Analytical methods based on inner-shell processes, such as x-ray fluorescence analysis or Auger spectroscopy, are using transition probabilities and branching ratios as fundamental parameters in their quantification procedures (e.g., Ref. [1]). On the other hand, the same parameters are also important for theoretical descriptions to account for many-electron correlations, such as double Auger processes (Ref. [2]).

The quantitative determination of the ratio of radiative to nonradiative and of single to double Auger transitions is difficult for several reasons. In the case of the ratio of radiative to nonradiative transitions, the quantitative analysis is hampered by the different detection techniques of photons and electrons. For the double Auger transitions, the main problem is encountered by the continuous energy distribution of the two simultaneously emitted electrons that makes it extremely difficult to distinguish them from background processes in an electron spectrum. Furthermore, for both cases, the angular distribution in the different decay processes must be taken into account.

All these difficulties do not exist when the photoelectron-photoion coincidence technique is used. The principle of the method is to identify a certain hole state as an initial state by means of measuring the kinetic energy of the photoelectrons [3,4]. The signal of the photoions measured in coincidence to the photoelectrons then shows the respective final ionic state. With this technique, the branching ratios of the decay routes of inner-shell hole states can be determined without the direct measurement of the double Auger electrons and the fluorescence photons emitted. Therefore, the problems with the different detection efficiency of photons and electrons and the continuous energy distribution of the double Auger electrons do not arise. As the photoions are detected by a 4π geometry, the different angular distributions of photons and electrons do not affect the measurements.

The photoion signals measured in coincidence, which have the same charge state as the initial state designated from the photoelectron, indicate the emission of a fluorescence photon. In contrast, the increase of the charge of the photoions by one or more in comparison to the initial state implies the emission of respective numbers of electrons. If the final ionic states are reached by direct transitions from the initial states, then the charge distribution of the photoions immediately gives the ratio of radiative to nonradiative and of single to double Auger transitions. For example, for elements with an atomic number less than 12, i.e., elements up to sodium, the branching ratio of the emission of fluorescence photons and of Auger electrons is obtained directly by the measurement of the coincident photoions into the portion with the same charge state (X^+) and into the portions with higher charge states (X^{n+}, $n>1$) with respect to the initial state. In the same way, the ratio of single to double Auger transitions is obtained by the ratio of X^{2+}:X^{3+}. If the final ionic states can be reached through intermediate states by cascade processes such as a photon transition with subsequent Auger decay or two subsequent Auger transitions (for example, the $1s^{-1}$ decay of elements with higher atomic numbers), additional information about these cascade transitions is needed and can be obtained by the same coincidence technique with the distinction that now the intermediate states are identified as initial states by the detection of the corresponding fluorescence photon or Auger electron.

In this work we investigate the decay of the neon 1*s* hole state after photoionisation with the photoelectron-photoion coincidence method and calculate the branching ratios with special emphasis on the probabilities of double Auger processes. The experiments were carried out at the U49/SGM beamline of the new electron storage ring BESSY II in Berlin, Germany. Synchrotron radiation with high flux and high resolution is provided by an undulator combined with a spherical grating monochromator. These characteristics

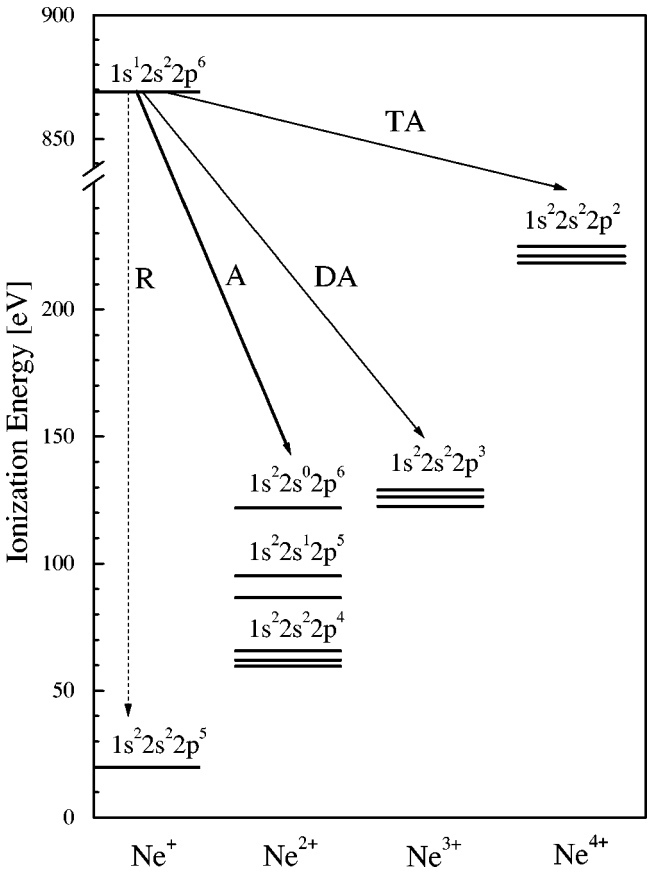

FIG. 1. Simplified energy level scheme for the neon 1*s* decay. Radiative transitions (R) are related to Ne^+, single Auger (A) transitions to Ne^{2+} double Auger transition (DA) to Ne^{3+}, and triple Auger transitions (TA) to Ne^{4+}.

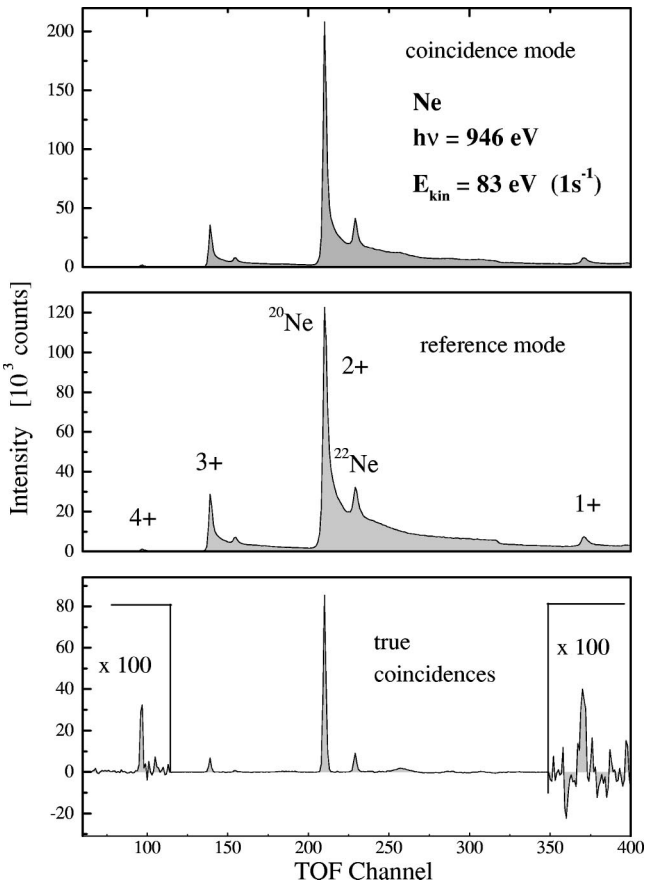

FIG. 2. Neon 1*s* coincidence measurements. Top: measured ion coincidence spectrum taken at 946 eV photon energy, containing true and false coincidences. Middle: corresponding reference spectrum of false coincidences. Bottom: spectrum of true coincidences evaluated with a method described in Ref. [6].

yielded reasonable count rates for the measurement of the Ne $1s^{-1}$ decay into the different final ionic states. Especially, the coincidence of the 1*s* photoelectron with the 1+ final ionic state, from which the fluorescence yield of the Ne *K* shell can be derived, could now be measured.

The experimental setup consists of a cylindrical mirror analyzer with which the photoelectrons are analyzed for their kinetic energy under the magic angle. Detected electrons trigger a high voltage pulse at a time-of-flight spectrometer (TOF) that extracts the corresponding coincident photoions into the TOF spectrometer. In the TOF spectrometer, the ions are separated by their mass to charge ratios. To account for false coincidences, a spectrum of random coincidences is also measured by triggering the ion extraction pulse randomly using a pulse generator. For further details of the experimental setup and the evaluation procedure, refer to [5,6]. In the case of neon, the measurement of the final ionic states leads directly to the different transition processes (Fig. 1): the radiative transition is related to Ne^+, the single Auger transition to Ne^{2+}, and the double Auger transition to Ne^{3+}. The production of Ne^{4+} is due to triple Auger transitions that include shake processes. Also, shake-off processes occur upon the radiative decay but can be neglected as calculations show. As the Auger effect is the main decay process, the measurement of the Ne^+ ions with a yield of about 1% as a result of fluorescence transitions needs a high precision in the measurement. We succeeded in determining the decay probabilities of Ne 1*s*, especially the fluorescence yield and the yield for the double Auger process, by photoelectron-photoion coincidence spectroscopy. Earlier investigations of Krause *et al.* [7] already used a coincidence technique but could not separate the electrons according to their energy. Thus, shake processes could not be separated preventing the exact determination of the branching ratios.

Figure 2 gives an example for a photoelectron-photoion coincidence measurement. The excitation energy was choosen to be 946 eV in order to omit near threshold effects such as post-collision interaction. The first two spectra from the top show the measured distribution of the final ionic charges of Ne in the coincidence and in the reference mode, respectively. The spectrum of true coincidences at the bottom of Fig. 2 is deduced from the coincidence spectrum and the reference spectrum, which represents the distribution of false coincidences. The spectra of true coincidences gained are then corrected for ion-detection efficiency, dead-time effects, and effects of event statistics. The results for the decay probabilities into the different final ionic states are tabulated in Table I, together with the values calculated.

The yields of the Ne^{i+} ions were calculated by the

TABLE I. Yields of the Ne^{i+} ions produced by the decay of the Ne $1s^{-1}$ state.

Ion charge	Experiment	Theory
1+	0.0096±0.0014	0.013
2+	0.9267±0.0021	0.956
3+	0.0597±0.0016	0.0305
4+	0.0038±0.0005	0.0005

straightforward construction of the deexcitation tree, considering radiative, Auger, and double Auger channels. Except for the double Auger branches during the *KLL* Auger decays, also monopole shake and double shake branches were considered for other transitions of the cascade. The respective branching ratios were calculated in the sudden limit [8]. The main focus in our calculations is laid upon many-electron correlations, which are accounted for within the configuration interaction method (CI). Although the electron correlation was long ago understood to be a reason of double Auger processes, only recently Amusia, Lee, and Kilin [2] were able to calculate within the lowest-order perturbation theory the partial width of the double process $1s^12s^22p^6$-$1s^22s^02p^5\epsilon_1 l_1 \epsilon_2 l_2$ in neon. In this work the probabilities of double Auger processes were calculated by considering the interaction of the final states of the core $(2s,2p)^{-2}$ by the excitations of either one or two electrons. One-electron excitations account for monopole double processes, i.e., shake processes, while two-electron excitations account for nonmonopole double processes. Only those two-electron excitations that are absent in the initial $1s^{-1}$ state were considered since it was found that the two-electron excitations that are present both in the initial and final state of an Auger transition (for example, $2p^2$-nl^2 excitations) lead to zero probabilities of multiple processes.

Figure 3 illustrates the mechanisms of double Auger processes in the neon atom. Since the double Auger final states $(2s,2p)^{-3}\{n,\epsilon\}l$—with an additional excited/ejected electron $\{n,\epsilon\}l$—contain the admixtures of the diagram $(2s,2p)^{-2}$ states, the amplitudes of the transitions $1s^{-1} \rightarrow (2s,2p)^{-3}\{n,\epsilon\}l$ are nonzero. The double Auger transition is ''direct'' if its final state contains the additionally excited electron in the continuum (ϵl). The transitions to the $2s^02p^5nl$ and $2s^12p^4nl$ states with an additional electron excited into a Rydberg state *nl* produce the 2+ ions. These are, however, short-lived and they eventually decay into the 3+ states via the $2s$-$2pnl$ transitions. This mechanism can be called a ''stepwise'' double Auger process. The Hartree-Fock orbitals optimized in the configuration $1s^{-1}$ are used for core orbitals in our CI calculations. In this work, the photoelectron is excluded from consideration, and the intermediate state of the core $1s^{-1}$ is regarded as a pure initial state undergoing decay. Each channel of electron excitation $\{n,\epsilon\}l$ containing states of the discrete (nl) and the continuous spectrum (ϵl) was represented by a single localized orbital optimized as it is described in [9]. Such orbitals are very much like natural orbitals used in extensive CI calculations [10]. As it is shown in [9], their use in the one-orbital-per-channel approximation allows one to account for about 90% of respective correlations.

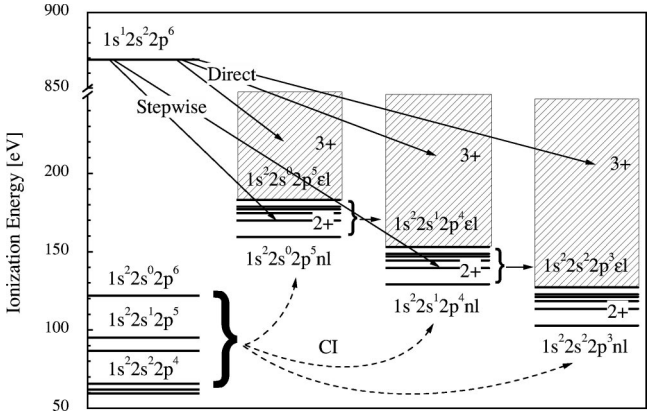

FIG. 3. Scheme explaining the mechanisms of double Auger processes in neon.

TABLE II. Calculated branching ratios for double Auger (DA) processes upon the decay of the Ne $1s^{-1}$ state.

Transition	Final state[a]	Process	Branching ratio (%)
KL_1L_1	$1s^22s^02p^6$	A	9.46
	$1s^22s^12p^4n,\epsilon s$	DA	0.14
	$1s^22s^12p^4n,\epsilon d$	DA	0.56
	$1s^22s^02p^5n,\epsilon p$	DA	0.14
KL_1L_{23}	$1s^22s^12p^5$	A	29.30
	$1s^22s^22p^3n,\epsilon s$	DA	0.25
	$1s^22s^22p^3n,\epsilon d$	DA	0.84
	$1s^22s^02p^5n,\epsilon s$	DA	0.03
	$1s^22s^12p^4n,\epsilon p$	DA	0.38
$KL_{23}L_{23}$	$1s^22s^22p^4$	A	58.24
	$1s^22s^02p^5n,\epsilon p$	DA	0.02
	$1s^22s^12p^42p^4n,\epsilon s$	DA	0.09
	$1s^22s^22p^3n,\epsilon p$	DA	0.55

[a]State giving the largest contribution in the CI wave function.

The double Auger channels considered and respective double Auger branching ratios are listed in Table II. Within the approximation employed, the double Auger processes are related to specific diagram Auger *KLL* transitions. It is interesting to note that various *KLL* transitions produce noticeably different amounts of the double Auger processes. As can be seen from Table II, less intense KL_1L_1 and KL_1L_{23} transitions provide the double Auger probabilities of 0.84% and 1.50%, respectively, while the most intense $KL_{23}L_{23}$ transition produces only 0.66%.

According to the calculations of Amusia, Lee, and Kilin [2], the probability of double Auger processes leaving the core in the configuration $1s^22s^02p^5$ is 1.5%. The authors [2] estimate that the partial contributions of the other transitions $1s^{-1} \rightarrow 2s^{-1}2p^{-2}\epsilon_1 l_1 \epsilon_2 l_2$ and $1s^{-1} \rightarrow 2p^{-3}\epsilon_1 l_1 \epsilon_2 l_2$ are of the same order of magnitude as the transition $1s^{-1} \rightarrow 2s^{-2}2p^{-1}\epsilon_1 l_1 \epsilon_2 l_2$, thereby obtaining a total double Auger probability of about 4%. This estimate is in sharp contradiction with our finding. Our calculations show that the contribution of $2s^{-2}2p^{-1}$ with 0.19% is much smaller than

those of $2s^{-1}2p^{-2}$ with 1.18% and $2p^{-3}$ with 1.64%. The main reason for these different contributions are the dipole polarization correlations $2s^{-2}\rightarrow 2s^{-1}2p^{-2}\{n,\epsilon\}\{s,d\}$ and $2s^{-1}2p^{-1}\rightarrow 2p^{-3}\{n,\epsilon\}\{s,d\}$ that mix strongly with the two hole states. A simple argument for the dominance of the contributions $2s^{-1}2p^{-2}$ and $2p^{-3}$ may also be seen in the statistical weights of the final states, where the ratio $2s^{-2}2p^{-1\,2}P_{3/2,1/2}:2s^{-1}2p^{-2\,2}S_{1/2}$, $^2D_{5/2,3/2}$, $^4P_{5/2,3/2,1/2}$, $^2P_{3/2,1/2}:2p^{-3\,2}D_{5/2,3/2}$, $^2P_{3/2,1/2}$, $^4S_{3/2}=6:30:20$ strongly prefers the contributions of $2s^{-1}2p^{-2}$ and $2p^{-3}$. Our calculated total double Auger probability is 3%. In comparison to earlier calculations [11], which included only monopole double shake processes, the inclusion of double Auger processes due to inner core correlations improves the agreement to the experimental values. Nevertheless, the yields of the Ne^{3+} and Ne^{4+} ions are still underestimated demanding even more elaborate calculations.

In conclusion, the photoelectron-photoion coincidence method used is shown to be a very promising method for the direct determination of the ratio of radiative and nonradiative transitions and the ratio of single, double, and triple Auger transitions in the decay of inner-shell hole states. Especially with respect to the fluorescence yields of the *K* shell of light elements, where only scarce data exist up to now, photoelectron-photoion coincidence measurements open up new ways to determine these essential parameters for modern analytical methods. In the case of the Auger transitions, the calculations of these ratios is a challenge for advanced many-body theories.

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