Auger emission from the resonantly excited $1s^1 2s^2 2p^6 3p$ state of Ne

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The 1*s* electrons of Ne have been ionized and excited to *np* ($n=3,4,\ldots$) Rydberg levels using monochromatized synchrotron radiation of mean energy 865 eV. The Auger spectrum resulting from the excited $1s^1 2s^2 2p^6 3p$ state has been studied both experimentally and theoretically by carrying out a detailed comparison with the spectrum resulting from the ionized $1s^1 2s^2 2p^6$ state. General agreement between the theoretical and experimental results is very good.

INTRODUCTION

Recently, the spectator-electron picture has been used successfully to explain the Auger decay structure in Ar, Kr, and Xe after resonant excitation of Ar 2*p*, Kr 3*d*, and Xe 4*d* electrons to Rydberg levels.[1–6] Theoretical calculations have been very successful in explaining energy shifts of the resonant Auger spectra. In addition, remarkably intense peaks have been observed for Kr and Ar due to the shakeup of the spectator electron during the Auger decay.[1–3]

To further our studies of resonant Auger processes,[1,2,6] it is a natural extension to study experimentally and theoretically the Ne 1*s* resonant Auger decay. The normal Auger spectra of Ne (used as the reference in the present work) have been widely studied in the past,[7–12] but this is the first time that the decay processes of the resonantly excited states have been investigated with good electron energy resolution. Recently, Kobrin *et al.*[13] have also studied threshold satellites of Ne but the energy resolution of their time-of-flight electron spectrometer was not good enough to resolve spectator and normal Auger spectra.

Relativistic Dirac-Fock calculations have been carried out for the energies and transition probabilities of normal Auger, spectator, shakeup, and participator processes. By comparing the results obtained by the same kind of calculations for both the $1s^1 3p \rightarrow (2s2p)^6 3p$ decay and the $1s^1 \rightarrow (2s2p)^6$ decay the influence of the 3*p* spectator electron has been determined in detail. The analysis is, furthermore, complemented by comparison with experiment. The importance of shakeup processes involving the spectator electron is demonstrated. The contribution of processes in which it is participating in the Auger decay is shown to be negligible.

EXPERIMENT

The measurements of the synchrotron radiation excited spectra were carried out using the Canadian Synchrotron Radiation Facility situated at the 1-GeV Aladdin storage ring in Stoughton, Wisconsin.[14,15] The beamline uses the Grasshopper Mark IV monochromator equipped with a 1200-groove/mm holographic grating. The electron spectra were taken with the Leybold-Heraeus electron spectrometer, applying a constant 100-eV pass energy.[16] The electron spectrometer contribution to the observed linewidths was about 0.8 eV, resulting in total Auger linewidths of ~ 1.0 eV. The electrons were detected at the magic angle of 54.7° so that the electron intensities are independent of the asymmetry parameter β and the polarization of the incident radiation.

Because of the relatively low photon resolution available from grazing incidence monochromateros at the high photon energies required (~ 870 eV), and the low cross sections [Ne 1*s* cross section[17] is only ~ 0.3 Mb above threshold—an order of magnitude lower than Ar 2*p* just above threshold (or Xe 4*d*)], it was not possible to selectively excite the Ne 1*s* to 3*p* or to 4*p* at 867.0 and 867.5 eV, respectively, or even to obtain the resonance Auger spectra free from the normal Auger spectra. The absolute minimum photon width in our monochromator at 810 eV is 2.5 eV (Ref. 14) with 10-μm slits. We had to use varying slit widths around 50 μm to obtain reasonable intensities, which gave us a photon width ~ 10 eV. In order to minimize the direct 1*s* ionization by the high-energy photons a slight lower mean photon energy than the resonance excitation energies was used. By means of total electron yield measurements it was found that a mean photon energy of 865 eV could be used to obtain a great deal of information on the resonant 1*s* to *np* Auger

spectra. Selective measurements would be extremely difficult with any existing monochromator that we are aware of.

THEORY

The transition energies and rates were calculated using the Dirac-Fock method. For the atomic and ionic many-electron bound states we used the multiconfigurational Dirac Fock (MCDF) code of Grant *et al.*[18] which easily accounts for the coupling between the core and the spectator electron as well as for the mixing of the *jj*-coupled configurations involved. Accordingly an atomic (ionic) state function (ASF) for a state i with total angular momentum JM is expanded in terms of the configuration state functions (CSF's). We have

$$\Psi_i(JM)=\sum_{\lambda=1}^{n} c_{i\lambda}\Phi_\lambda(JM)\ , \tag{1}$$

where n is the number of CSF's included in the expansion and $c_{i\lambda}$ are the mixing coefficients for state i. In the calculation of the initial state we included all *jj*-coupled configurations resulting from the nonrelativistic $1s2s^22p^6$ and $1s2s^22p^63p$ configurations for the ordinary and resonant Auger transitions, respectively. This is effectively an intermediate coupling calculation for the initial state. For the ionic final state of the ordinary Auger transition we included all *jj*-coupled configurations which result from the nonrelativistic $1s^22p^6$, $1s^22s2p^5$, and $1s^22s^22p^4$ parent configurations. The parent configurations for the resonant case were obtained by adding a $3p$ orbital to each of the previous configurations. Separate self-consistent-field (SCF) calculations of the initial- and final-state energies were carried out using an average level optimization scheme.[18] The transition energies were obtained as their difference ($\Delta E_{\rm SCF}$ approach). The total wave function of the final state describing the system of an ion plus an Auger electron was obtained by coupling the continuum orbital of the Auger electron to the corresponding ionic state wave function. The interaction between the continuum channels was, however, not taken into account. The continuum orbitals were calculated in the average *jj* potential of the initial-state configurations by keeping the bound orbitals fixed. Lagrangian multipliers were included to enforce orthogonality between the bound orbitals and the continuum orbital.

The transition rates were calculated using first-order perturbation theory. This implies a two-step model in which the primary excitation of the atom is assumed to take place independently of the decay.[19] This excludes such effects as the resonant Raman effect[20] and the post-collision interaction (PCI).[21,22] Assuming energy normalization for the continuum orbital of the Auger electron $|\epsilon ljm\rangle$ the Auger component transition probability from a single-vacancy initial state i to any double-vacancy final state f is given by

$$T_{if}=\frac{2\pi}{\hbar}\sum_j\left|\sum_\lambda\sum_{\lambda'}c_{i\lambda}c_{f\lambda'}\left\langle\Phi_{\lambda'}(J'M')\epsilon lj;JM\left|\sum_{\mu,\nu}V_{\mu,\nu}\right|\Phi_\lambda(JM)\right\rangle\right|^2\ , \tag{2}$$

where J and J' are the total angular momenta for the initial and final ASF's respectively. In Eq. (2) the two-electron operator $V_{\mu,\nu}$ was taken to be the sum of the Coulomb and transverse Breit operators given by

$$V_{\mu,\nu}=\frac{1}{r_{\mu,\nu}}-(\underline{\alpha}_\mu\cdot\underline{\alpha}_\nu)\frac{e^{i\omega r_{\mu,\nu}}}{r_{\mu,\nu}}+(\underline{\alpha}_\mu\cdot\nabla_\mu)(\underline{\alpha}_\nu\cdot\nabla_\nu)\frac{e^{i\omega r_{\mu,\nu}}-1}{\omega^2 r_{\mu,\nu}}\ , \tag{3}$$

where $\underline{\alpha}_\mu$ are Dirac matrices and ω the frequency of the virtual photon.[23] Some transition rates were also calculated using other forms of electron-electron interaction, connected to operator (3) by a gauge transformation. The gauge dependence was, however, found to be small. The many-electron matrix element (2) was reduced into a sum over two-electron Slater integrals using angular momentum coefficients given by the MCDF code.[18] The bound orbitals used in the calculation of the radial two-electron integrals were taken from the SCF calculation of the initial state. This neglects the relaxation of the orbitals in the Auger process.[19]

DISCUSSION

The experimental spectrum in the kinetic energy region of 745–816 eV is shown in Figs. 1(a) and 2(a). A fit of 15 Voigt functions with the use of the computer code CRUNCH (Ref. 24) yields the lines indicated by the vertical bars. Due to the low counting rate and rather low statistics it was not possible to include individual linewidths in the fitting procedure with sufficient accuracy. Consequently the same width and shape of the Voigt functions were used throughout the fitting of the spectrum. The success of the fit indicates that the changes in the absolute transition rates are minimal for different decay modes. Hence it is meaningful to compare the line intensities and energies with the theory.

With the large bandwidth used, the ionization of the $1s$ electron as well as the excitation of it to the vacant $3p$ and higher np orbitals are simultaneously possible. The resulting $1s^12s^22p^6$ hole states and $1s^12s^22p^63p^1$ excited states decay with a probability of about 98.2% by Auger transitions. Peaks 1, 4, 7, 10, and 12 in Figs. 1(a) and 2(a) are due to the

$$1s^12s^22p^6\rightarrow 1s^22s^02p^6+1s^22s^12p^5+1s^22s^22p^4$$

normal Auger transitions in accordance with earlier studies.[7-12] Within the accuracy of the experiment the measured energies and relative intensities of these transitions are in a good agreement with those reported earlier[7-12] and are therefore not listed here. As shown in Figs. 1(a) and 2(a) each normal Auger peak (denoted by A in the following) is accompanied by two peaks at 1.5±0.3 eV (denoted by C) and 6.6±0.4 eV (denoted by B) higher kinetic energy (e.g., peaks 2 and 3, 5 and 6, 8 and 9, 11 and 14, 13 and 15). The B and C transitions most likely involve the excited $3p$ electron. It has been found in other rare-gas studies[1-4] that normally the transition energies are shifted towards higher kinetic energy due to the shielding of the Auger electron by the spectator electron. In the following we shall identify B as

$$1s^1 2s^2 2p^6 3p^1 \rightarrow 1s^2 (2s2p)^6 3p^1$$

spectator transitions and C as

$$1s^1 2s^2 2p^6 3p^1 \rightarrow 1s^2 (2s2p)^6 4p^1$$

shakeup transitions.

We start by considering our calculations of the energies and transition probabilities for the normal and $3p$ spectator Auger processes. It was found that the two-electron radial integrals for these two processes agree within 1% with each other. Thus the total Auger transition rates for the decay of the $1s2s^2 2p^6$ and $1s2s^2 2p^6 3p$ states were found to be 10.399×10^{-3} and 10.357×10^{-3} a.u., respectively. The close resemblance of the corresponding spectra is demonstrated in Figs. 1(b) and 2(b). In these figures the profiles of the normal (A), $3p$ spectator (B), and $3p$ to $4p$ shakeup (C) spectra were obtained by superposition of Lorentzians with widths equal to the experimental one, and positions equal to the calculated transition energies. The heights of the peaks within each group were put equal to the calculated relative transition rates. The relative heights of the three profiles A, B, and C were adjusted to agree with the intensity ratios of peaks 12, 15, and 13 of experiment, respectively. Our analysis shows in comparison with Figs. 1(a) and 2(a) that the spectator and shakeup spectra are uniformly shifted and reduced by a constant factor with respect to the normal spectrum.

The calculated $3p$ spectator transition (B) energies and relative intensities agree well with those of experimental peaks 3, 6, 9, in Fig. 1(a) and 14 and 15 in Fig. 2(a). Theory predicts an overall shift of 6.7±0.3 eV between the normal and $3p$ spectator Auger spectra. This agrees well with the energy difference of 6.6±0.4 eV between the peaks 3, 6, 9, 14, and 15 and the normal Auger peaks 1, 4, 7, 10, and 12 in the experimental spectra. Due to the coupling between the core and the spectator electron the number of energy levels both in the initial and final state of the decay increases from that of the normal levels, being four ($1s_{1/2}3p_{1/2}$, $J=0,1$ and $1s_{1/2}3p_{3/2}$, $J=1,2$) in the initial state and 41 in the final state. Therefore the number of lines in the spectator spectrum increases drastically compared to the normal spectrum. However, lines corresponding to the transitions between the daughter levels of a given parent level of the normal configuration are energetically so close to each other [all the

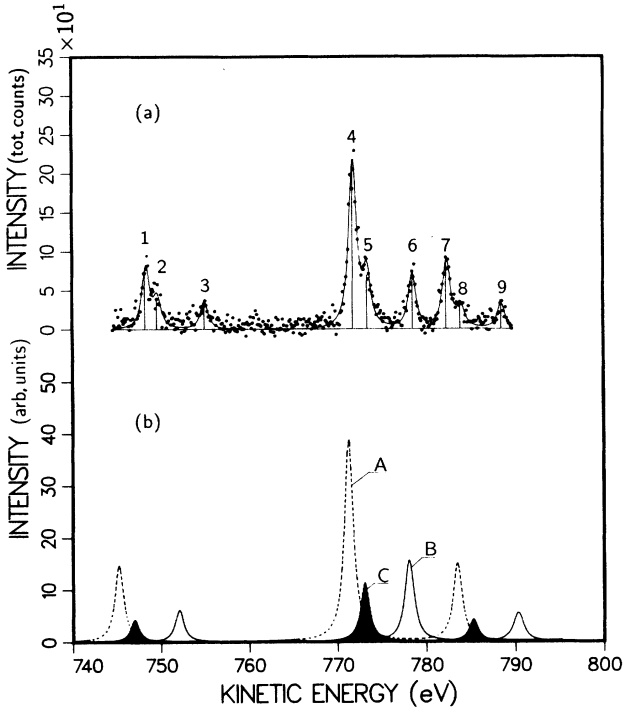

FIG. 1. (a) Experimental KL_1L_1 and $KL_1L_{2,3}$ spectra of Ne recorded after ionization or excitation of the $1s$ electrons at 865-eV photon energy. The solid line is the result of the fitting procedure as explained in the text. (b) Calculated profiles of the (A) $1s^1 \rightarrow 2s^0 2p^6 + 2s^1 2p^5$ transitions (dashed line); (B) $1s^1 3p \rightarrow (2s^0 2p^6 + 2s^1 2p^5)3p$ transitions (solid line); and (C) $1s^1 3p \rightarrow (2s^0 2p^6 + 2s^1 2p^5)4p$ transitions (shaded area).

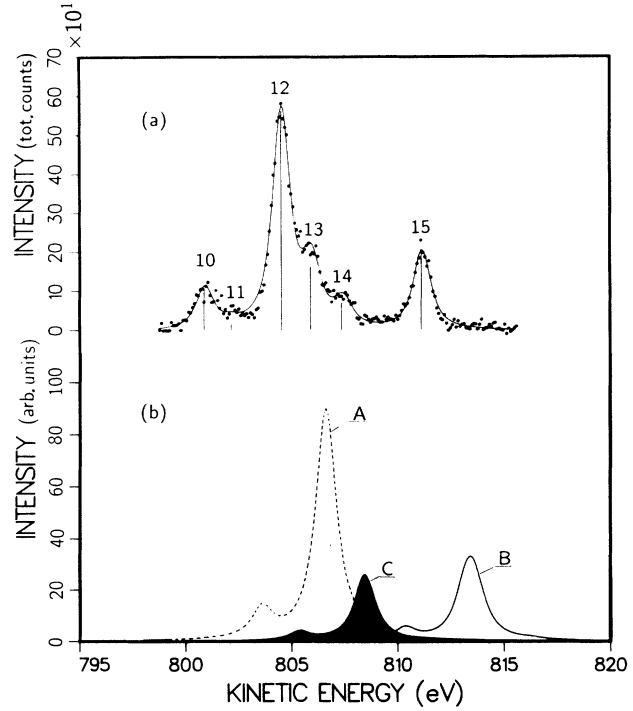

FIG. 2. (a) Experimental $KL_{2,3}L_{2,3}$ spectrum of Ne. (For an explanation, see Fig. 1.) (b) Calculated profiles of the (A) $1s^1 \rightarrow 2p^4$ transitions; (B) $1s^1 3p \rightarrow 2p^4 3p$ transitions; and (C) $1s^1 3p \rightarrow 2p^4 4p$ transitions.

$2p^4(^1G_4)3p$ daughter levels fall within 0.5 eV, for example] that they are not resolved in the present experiment. The open-shell structure of the initial and final spectator configurations only manifests itself in a broadening of the peaks. As shown in Figs. 1(b) and 2(b), the spectator peaks labeled *B* are somewhat broader than the normal Auger peaks labeled *A* although the same linewidth was used for each component line in the construction of these spectra. Such a trend is also discernible in the experimental spectra in Figs. 1(a) and 2(a). The splitting is largest ($\sim$1 eV) for the $2p^4(^3P)3p$ daughter levels, but the transitions to these levels have such a low intensity that they do not show up in the spectrum.

The positions of the peaks 2, 5, 8, in Fig. 1(a) and 11 and 13 in Fig. 2(a) are in a good agreement with calculated energies of the transitions where a $3p$ to $4p$ shakeup during Auger decay has been assumed [profile *C* in Figs. 1(b) and 2(b)]. According to our calculations the $3p$ to $4p$ shakeup lines are shifted by about 5.0 eV towards lower energies with respect to the $3p$ spectator lines or 1.7 eV to higher energies from the normal Auger lines. This agrees well with the observed shift of 1.5±0.3 eV of the peaks 2, 5, 8, 11, and 13 from the normal Auger lines. The decay from higher spectator states ($n \geq 4$) should appear as separate peaks since according to our calculations the energy difference between the $3p$ and $4p$ spectator line is 3.2 eV. However, no significant structure is found at these energy positions (e.g., between peaks 5 and 6 or 8 and 9). At first sight this result seems strange since the ratio of the $1s \rightarrow 4p$ to $1s \rightarrow 3p$ photoabsorption cross sections is as large as 0.4 according to quantum-defect theory estimates.

The collapse of $3p$ and $4p$ orbitals on going from the initial $1s^12s^22p^63(4)p^1$ state to the final $1s^2(2s2p)^63(4)p^1$ state makes it possible that these electrons will shake to neighboring orbitals. Figure 3 shows the radial charge densities of the $3p$, $4p$, and $5p$ Rydberg electrons before and after the Auger decay and Table I the squares of the relevant overlap integrals. The initial and final orbitals were calculated in average potentials of the $1s2s^22p^6$ and $1s^2(2s2p)^6$ core states, respectively. The radial densities and overlap integrals were found to be rather insensitive to the coupling of the ionic core. Shakeup processes involving core electrons during the Auger decay have been found to be of minor importance in the case of normal Auger transitions in earlier studies.[25] For the spectator electron, however, anomalously strong shake probabilities have been obtained recently in other rare gases.[1-6]

If peaks 2, 5, 8, 11, and 13 are assigned to the $1s^12s^22p^63p^1 \rightarrow 1s^2(2s2p)^64p^1$ transitions, an average branching ratio of 1.5 follows for the $3p$ spectator to shakeup spectrum. This is somewhat smaller than the estimate 2.5 based on the overlap integrals in Table I. The large values of $|\langle 4p|np\rangle|^2$ ($n \neq 4$) shake probabilities also explain why there are no $4p$ spectator lines in the spectrum. According to Table I the $1s2s^22p^64p$ states decay predominantly to the neighboring state by either shakeup or shakedown transitions. The corresponding lines intermingle with the $3p$ spectator and normal spectrum. At photon energies close to the threshold, post-collision interaction effects[20-22] may result in asymmetric line shapes. Due to the wide photon bandwidth used in this experiment and due to the low statistics, no significant asymmetries could be associated with the PCI effect. This is natural since the lifetime width of the $1s$ hole is only about 0.2 eV in neon and this makes the PCI shifts and asymmetries rather small.

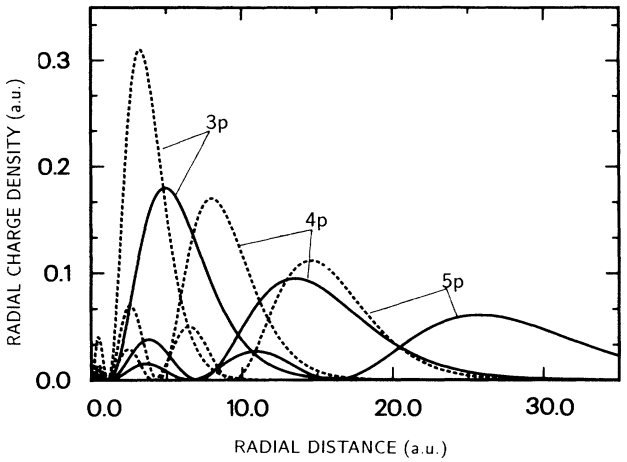

FIG. 3. Radial charge densities of the $3p$, $4p$, and $5p$ Rydberg electrons computed in the field of the $1s2s^22p^6$ and $1s^2(2s2p)^6$ configurations, respectively. The solid lines correspond to the Ne^+ configuration and the dashed lines to the Ne^{2+} configuration.

The theoretical absolute transition rates of the participator processes

$$1s^12s^22p^63p^1 \rightarrow 1s^22s^22p^5$$

and

$$1s^12s^22p^63p^1 \rightarrow 1s^22s^12p^6$$

were found to be 0.018×10^{-3} and 0.005×10^{-3} a.u., respectively. These are much lower than the spectator transition probabilities and hence the spectator Auger decay is the dominant decay mode of the resonantly excited states in Ne. For Ar, the participator process was also calculated by Hansen[26] to be of minor importance. The same was observed experimentally for Kr and Xe by measuring the outer-shell *ns* and *np* photoelectron spectra in the resonance photon energy region.[3,4] The observed variations caused by participator decay were found to be small.

TABLE I. Shakeup (shakedown) probabilities for various spectator states.

n	$\lvert\langle 3p\lvert np\rangle\rvert^2$	$\lvert\langle 4p\lvert np\rangle\rvert^2$
3	0.715	0.086
4	0.282	0.260
5	0.001	0.639
6	0.001	0.014
7	0.000	0.000

In conclusion, the Ne 1s resonant Auger electron spectrum has been obtained at a mean photon excitation energy of 865 eV. In addition to the normal Auger spectrum two distinct groups of lines have been observed. Using relativistic Dirac-Fock calculations they have been shown to result from $1s^{1}3p \rightarrow (2s2p)^{6}3p$ spectator and $1s^{1}3p \rightarrow (2s2p)^{6}4p$ shakeup transitions. It is indicated that the 4p spectator structure is weak due to 4p shakedown and shakeup processes.

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