Coster-Kronig Transitions in Hollow Atoms Created during Highly Charged Ion-Surface Interactions

J. Limburg, J. Das, S. Schippers, R. Hoekstra, and R. Morgenstern
Kernfysisch Versneller Instituut, Zernikelaan 25, 9747 AA Groningen, The Netherlands

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We present high resolution KLL Auger spectra emerging from collisions of H-like and metastable He-like C, N, and O on a B-doped Si(100) surface. In combination with the high resolution electron spectroscopy, Hartree-Fock calculations allow us to succesfully identify KLL Auger electrons arising from specific states that form a part of the autoionization cascade as the multiply excited projectiles deexcite. We find strong evidence for Coster-Kronig transitions taking place in the hollow atoms which give rise to missing peaks in the Auger spectra.

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The field of highly charged ion-surface collisions research has grown rapidly during the last few years. The vast amount of potential energy carried by highly charged ions holds the promise of possible technological applications based on creating nanometer-sized surface modifications, especially of semiconductor and insulator surfaces [1]. In this context it is of great importance to know the potential energy of the ions upon hitting the surface. Electron spectroscopy of Auger electrons emitted during collisions of multicharged ions with surfaces is a sensitive tool for probing the state of the ion when it impinges on the surface.

It is well established [2–6] that in the early stages of the collision process, prior to collision with the surface, multiply excited neutral atoms with empty or sparsely populated inner shells are formed. This is due to electron capture from the target occurring mainly via resonant neutralization into high-lying Rydberg states of the projectile. It is also known that these atoms start to deexcite by means of autoionization processes (AI) [7] but the slow rates of autoionization do not allow a complete relaxation of the projectiles prior to collision with the surface. A significant fraction of inner shell vacancies is therefore carried into the surface and filled only after the projectile has suffered close encounters with the target atoms [2,8]. But the exact deexcitation pathways are still not clear. Neither the states primarily populated nor the individual transitions contributing to the autoionization cascade are precisely known.

In this Letter we present high resolution electron energy spectra of hydrogenlike C^{5+}, N^{6+}, and O^{7+} and of heliumlike ($1s2s$ core) C^{4+}, N^{5+}, and O^{6+} metastables colliding with a Si(100) target. The differences between the spectra of the hydrogenic ions and the metastables allow us to track the sequence of the AI cascade and to identify distinct states populated prior to the emittance of the K Auger electron. The shape of the spectra is determined mainly by the presence or absence of Coster-Kronig transitions in the particular hollow atom under consideration.

The electron spectra were measured in an ultrahigh-vacuum collision chamber with a base pressure well below 2×10^{-8} Pa. The multiply charged ion beams were extracted from the Kernfysisch Versneller Instituut at Groningen electron cyclotron resonance (KVI-ECR) ion source and then transported to the experimental setup. Floating the complete apparatus on a positive voltage allowed us to decelerate the ion beam from the ECR source to the desired collision energy. The target used for the experiment was a B-doped Si(100) crystal. The target was sputter cleaned with Ar ions and annealed prior to each measurement and the surface cleanness was monitored by using low energy recoil ion spectroscopy. The electron detector was a 180° spherical electrostatic analyzer equipped with a channeltron and rotatable over a large range of detection angles. The energy resolution of the analyzer is $\Delta E/E = 0.5\%$ and its acceptance at the center of the target is $11.2 \times 10^{-8}E$ (sR eV), with E being the energy of the detected electrons in eV. A more detailed description of the apparatus has been presented elsewhere [6].

Figures 1(a)–1(c) show K Auger spectra (corrected for analyzer transmission and background subtracted using an algorithm according to Shirley [9]) measured during collisions of 250 eV $C^{4+/5+}$, $N^{5+/6+}$, and $O^{6+/7+}$ with a Si(100) surface. An increase of resolution in the relevant parts of the spectra was obtained by using an energy window in which the step length between successive points was decreased and the measuring time was increased, yielding better statistics. All spectra are characterized by the presence of a broad structure with sharp peaks superimposed on it. This broad underlying structure, the relative importance of which increases with increasing collision energies, has previously been identified as arising from electrons emitted by the projectiles from inside the top few surface layers of the target while the narrow peaks are assigned to electrons that are emitted above the surface. Information about the projectile velocity at the moment of electron emission can be gained from measurements at different detection angles which reveal a Doppler shift of the various peaks [2,8,10].

Measurements of the strong peaks in hydrogenic nitro-

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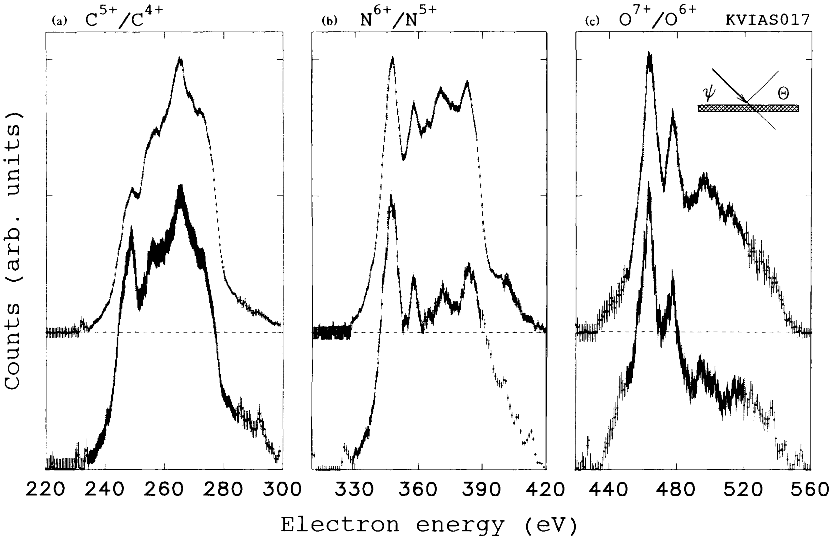

FIG. 1. (a), (b), and (c): Electron energy spectra arising from collisions of 250 eV ($\psi = 15°, \theta = 90°$) hydrogenic (upper spectra) and heliumlike (lower spectra) carbon, nitrogen, and oxygen on Si(100). In the relevant parts of the spectra the sampling time per channel is increased to improve the statistics.

gen and oxygen as a function of the emission angle show that the two sharp peaks at 347 and 358 eV in nitrogen and at 464 and 478 eV in oxygen [Figs. 1(b) and 1(c)] indeed exhibit a Doppler shift in accordance with ions moving along the incident direction [11]. This has earlier been demonstrated for N^{6+} projectiles in more detail [10]. The narrow width of these above the surface peaks indicates that they arise from specific initial configurations in contrast to the broad subsurface structure which contains contributions from a whole variety of initial configurations [12].

In order to identify the transitions that give rise to these peaks we have performed Hartree-Fock calculations using the COWAN code [13]. Table I lists the KLL energies and transition rates for all possible configurations with two electrons in the L shell, for C, N, and O atoms. In one set of our HF calculations, we have assumed that the L shell contains two electrons, and that the rest of the electrons are in the M shell, in configurations $3s^x3p^y$ where $x+y$ is 3, 4, and 5 for C, N, and O, respectively. The work function of the Si target is on the order of 5 eV, so in the calculation a contribution of $3d$ electrons ($E_b \simeq 2$ eV) can be omitted. For brevity we will omit in the following the 3ℓ electrons from the notation and label the configurations as $1s2\ell2\ell'$. Using the calculated transition energies and rates we have constructed simulated spectra. These have been used to estimate theoretical intensity ratios of the $1s2s^2$, $1s2s2p$, and $1s2p^2$ peaks. A more detailed description of these HF calculations and the construction of simulated spectra will be given in a forthcoming publication by Schippers *et al.* [14].

Comparison of the experimentally measured spectra with the calculated energies given in Table I indicates that the two low energy peaks in the various spectra arise from initial states $1s2s^2\,{}^2S$ and $1s(2s2p\,{}^3P)\,{}^2P$, respectively. Regarding the peak assignment Andrä *et al.* [15] have recently come to a similar conclusion regarding the first KLL Auger peak. The second peak, however, is assigned—different from their earlier tentative suggestion [3] to a configuration with 3 L electrons. Regarding intensities some striking differences can be observed when one compares the spectra from hydrogenic projectiles with their He-like counterparts. For metastable projectiles the contribution of the two low-energy peaks compared to the total intensity much larger as for H-like ones. This can be understood from the fact that for the initial ($1s2s$) configuration in the metastables the formation of a $1s2s^2$ or $1s2s2p$ configuration is much more probable than that of $1s2p^2$ which would need a s to p jump of the initial $2s$ electron. In the H-like spectra a sizable contribution can be expected from $1s2p^2$ states, which contribute to the higher energy part of the KLL Auger spectrum. In the hydrogenic C and N spectra peaks arising from $1s2p^2$ configurations [$1s(2p^2\,{}^1D)\,{}^2D$ at 265 and 369 eV] are indeed observed, but calculations show that at these energies there are also contributions from KLL Auger electrons originating from configurations with more than two L-shell electrons. This makes a clear separation of the $2p^2$ peaks from other contributions impossible.

But for oxygen there is certainly no evidence for a $2p^2$ contribution [$1s(2p^2\,{}^1D)\,{}^2D$ predicted at 490 eV]. Since the L shell is populated via both the AI cascade and direct capture from the surface it is reasonable to assume that all the states arising from $1s(2\ell)^2$ parent configurations are populated. The absence of the $2p^2$ peaks implies the presence of a mechanism in O^{7+} that inhibits the "depopulation" of the $2p^2$ configurations via KLL Auger decay.

Before tackling this problem it should be mentioned that the majority of KLL Auger transition rates are significantly larger than 10^{13} s^{-1} [16]. So in order to inhibit the depopulation of the $2p^2$ configurations via KLL Auger, we need a mechanism with much faster rates (i.e., $\Gamma \geq 10^{15}$ s^{-1}) than the KLL transition rates at-

TABLE I. *KLL* Auger energies and peak intensities (normalized to the $1s2s^2$ configuration). *KLL* energies (E) are in eV. All measured peak positions coincide with the calculated positions, assuming remaining electrons in the M shell, within an error range of 2 eV. The column "No C-K" gives the peak intensities calculated using simulated spectra, and the column "C-K" gives the peak intensities under assumption that Coster-Kronig transitions occur whenever the energy difference between configurations exceeds 5 eV. The column "Expt" gives the measured peak intensity ratios. Errors in these estimates are on the order of 20%. Intensities labeled * cannot be deconvoluted; see text.

	Configuration	E	No C-K	C-K	Expt	E	No C-K	C-K	Expt	E	No C-K	C-K	Expt
							Primary ion						
			Carbon C^{5+}				Nitrogen N^{6+}				Oxygen O^{7+}		
A	$1s(2s^2\,{}^1S)\,{}^2S$	248	1.0	1.0	1.0	347	1.0	1.0	1.0	464	1.0	1.0	1.0
B	$1s(2s2p\,{}^3P)\,{}^2P$	256	1.0	0.26	0.25	358	1.12	0.27	0.30	478	0.85	0.24	0.25
C	$1s(2s2p\,{}^1P)\,{}^2P$	262	2.34	···	···	364	2.51	···	···	484	2.23	···	···
D	$1s(2p^2\,{}^3P)\,{}^2P$	261	0.71	0.6	*	363	2.62	0.64	*	484	1.57	···	···
E	$1s(2p^2\,{}^1D)\,{}^2D$	265	7.34	1.9	*	369	6.00	1.46	*	490	5.94	···	
F	$1s(2p^2\,{}^1S)\,{}^2S$	271	0.52	···	···	376	0.60	···	···	498	0.93		
							Primary ion						
			Carbon C^{4+}				Nitrogen N^{5+}				Oxygen O^{6+}		
A	$1s(2s^2\,{}^1S)\,{}^2S$	248	1.0	1.0	1.0	347	1.0	1.0	1.0	464	1.0	1.0	1.0
B	$1s(2s2p\,{}^3P)\,{}^2P$	256	1.0	0.30	0.30	358	1.12	0.32	0.35	478	0.85	0.27	0.30
C	$1s(2s2p\,{}^1P)\,{}^2P$	262	2.34	···	···	364	2.51	···	···	484	2.23	···	···

tached to these configurations. Coster-Kronig processes can occur on these very short time scales, Cowan calculations give C-K rates 10 to 100 times larger than the relevant *KLL* rates. Coster-Kronig transitions are intrashell Auger transitions in which the rearrangement of electrons in an inner shell leads to emission of an outer electron, for example, $(1s2p^2\,3\ell^5) \rightarrow (1s2s2p\,3\ell^4) + e^-$. Assuming that the binding energy of the outermost captured electrons is on the order of 5 eV, i.e., the work function of the target, the rearrangement of inner shell electrons has to yield at least this amount of energy in order to allow a Coster-Kronig transition. Since binding energies and their separations for different states—and thus also the energy gain upon electronic rearrangement—increase with Z one can expect that Coster-Kronig transitions will become energetically possible for a certain Z. Inspection of the calculated energies (see Table I) shows indeed that for oxygen the energy difference between states having a $1s(2p^2\,{}^1D)\,{}^2D$ or a $1s(2s2p\,{}^1P)\,{}^2P$ core is 6 eV. Hence for O^{7+} projectiles the corresponding *LLM* Coster-Kronig transitions are allowed and may act as a fast depopulation mechanism for the $1s(2p^2\,{}^1D)\,{}^2D$ cores. Note that states with a $1s(2s2p\,{}^1P)\,{}^2P$ core fed in this way can on their turn decay via a Coster-Kronig *LLV* transition to ones with a $1s2s^2$ core. Therefore the corresponding peak is also absent in the *KLL* spectra, whereas the $2s2p\,{}^3P$ term, being stable against Coster-Kronig transitions due to spin conservation, is observed in the spectra. Assuming that energy differences above 5 eV suffice for a Coster-Kronig transition and that spin is conserved one can predict that all oxygen cores with two L electrons are transformed into $1s2s^2$ or $1s(2s2p\,{}^3P)\,{}^2P$ states via Coster-Kronig transitions, and that *KLL* Auger electrons can only be observed from these two states. This is in accordance with the measured oxygen spectra [Fig. 1(c)].

However, turning to the case of C^{5+} and N^{6+} the energy difference between $1s(2p^2\,{}^1D)\,{}^2D$ and $1s(2s2p\,{}^1P)\,{}^2P$ is only 3 to 4 eV. This is too small an energy difference for the proposed *LLM* Coster-Kronig transitions to proceed. Therefore the only possible Coster-Kronig transitions in C and N are from $1s\,(2p^2\,{}^1S)\,{}^2S$ to $1s\,(2s2p\,{}^1P)\,{}^2P$ and from $1s\,(2s2p\,{}^1P)\,{}^2P$ to $1s\,(2s^2\,{}^1S)\,{}^2S$. In reality the stepwise variation in the occurrence of C-K transitions in O as opposed to C and N will be a smoother one from C via N to O due to the possibility that a rearrangement of

M-shell electrons might give rise to electrons which are bound by only 3 to 4 eV.

To estimate the relative intensities of the various peaks we assume that all possible core states are primarily populated according to their statistical weight. Taking their decay rates into account direct KLL transitions then yield intensities which are indicated in Table I in the column "No C-K." Assuming, however, that decay via Coster-Kronig transitions proceeds whenever this is possible ($\Delta E > 5$ eV) yields relative intensities given in the "C-K" column. The intensities $A_{\text{C-K}}$ to $F_{\text{C-K}}$ of the peaks A to F with inclusion of Coster-Kronig transitions, is calculated from the "pure" intensities as follows: $A_{\text{C-K}} = A + C + F$ for carbon and nitrogen; $A_{\text{C-K}} = A + C + E + F$ and $B_{\text{C-K}} = B + D$ for oxygen. All intensities are normalized to the $1s2s^2$ (A) configuration. The determination of the experimental intensities as listed in the column "Expt" will be discussed in more detail in [11]. However, the approximate agreement of the "C-K" intensities with those estimated from the experimental spectra is a strong support of the interpretation based on the occurrence of Coster-Kronig transitions.

It should be noted that the mechanisms discussed here can be active above and below the surface. New aspects regarding above and below surface emission of KLL Auger electrons are discussed in more detail in [11] and [14].

In conclusion, it can be said that we have successfully identified, for the first time, individual KLL Auger transitions that form part of the AI cascade as the multiply excited hollow atom deexcites to the ground state. This unambiguous identification of specific KLL transitions not only contributes towards a more accurate interpretation of low resolution Auger spectra but also provides important details required for theoretical models of the ion-surface interaction dynamics. We find that Coster-Kronig transitions play an important role in determining the shape of the K Auger spectra. In systems where these fast transitions are energetically possible they move the population of certain initial states giving rise to "missing" peaks in the KLL spectra. A target with a work function below 3 eV will enable the "forbidden" Coster-Kronig transitions in C and N and the use of such a target will therefore be an interesting test of the above described theory.

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