L Auger electron production in 0.3–3.2-MeV krypton ion-atom collisions

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Secondary electron production as a consequence of inner-shell vacancy decay for the Kr-Kr system has been studied. Electron-energy spectra differential in impact parameter have been obtained by detecting electrons in coincidence with projectile ions scattered through a known angle. The spectra exhibit structure attributable to Auger decay of L-shell vacancies. The collision-energy dependence of the L Auger yields is consistent with the L-shell excitation being due to rotational coupling of the $4f\sigma$, $4f\pi$, $4f\delta$, and $4f\varphi$ orbitals of the Kr-Kr quasimolecule, as originally proposed by Shanker and co-workers. The L Auger electron energies and relative transition-group intensities suggest that L-shell vacancy decay occurs in Kr ions with initial charge states greater than $+10$, indicating that a surprisingly large number of electrons are emitted prior to the decay of the L-shell vacancy. These prior ionizations, most of which occur during the collision, are the source of the 100–800-eV continuum electrons that dominate the low-energy region of the electron spectrum.

I. INTRODUCTION

Quasimolecular excitation mechanisms in atomic collisions have been used to explain inner-shell vacancy production in collisions of heavy ions with heavy atoms, since the discovery in the mid 1960s of unexpectedly large cross sections for inner-shell excitation. The historical development has been summarized, in several review articles.[1] Initially, research focused on understanding impact-parameter-dependent thresholds for inner-shell vacancy production, and comparing data with potential-energy diagrams for one-electron orbitals formed in the quasimolecule during the collision. More recently, attempts have been made to explain the origin of continuum electrons (100–800 eV) with the quasimolecular model.[2–6]

Vacancy production probabilities may be determined experimentally in a variety of ways, including measurement of the collision's inelastic energy loss and spectroscopy of x rays and secondary electrons produced by vacancy decay. The x-ray method is the most widely used of these techniques; but it has the shortcoming of requiring a knowledge of the fluorescence yield, defined as the ratio of the number of vacancies decaying radiatively to the number of inner-shell vacancies actually produced by the collision. Since the fluorescence yield depends upon the electron configuration following the collision, the x-ray technique does not always yield unambiguous results. The Auger technique does not suffer from this difficulty—in fact, the Auger-electron energies are a sensitive *measure* of ionization taking place during the collision (i.e., prior to L vacancy being filled). Auger spectroscopy is, therefore, an important resource for the understanding of vacancy production. This paper is a presentation of experimental results and data analysis for the Kr-Kr collision system using electron-energy spectroscopy of L-shell vacancy decay and provides new insight into the ionization process in Kr-Kr collisions.

II. APPARATUS

The Kr projectile beam is produced in the terminal of a 2-MV Van de Graaff accelerator. The doubly or singly ionized Kr projectile ions are mass analyzed and directed into a 42-cm-diam scattering chamber. The Kr target gas effuses into the chamber through a 0.1-mm-i.d. (inside diameter) steel needle at a rate of about 1×10^{16} atoms per second. The projectile beam is collimated to pass through the target gas, thus localizing an area of high-collision frequency. Auger electrons created by the collision are detected by a cylindrical electrostatic energy analyzer with 4% full width at half maximum resolution.[7] The Auger-electron emission is assumed nearly isotropic in the center-of-mass frame, so electron detection angle was chosen to be 90° simply to minimize kinematical (Doppler) energy shifts.

For the ion-electron coincidence experiment described in Sec. IV, the ion-scattering angle is defined by passing the scattered ions through annular collimaters coaxial with the incident beam. These ions strike a conical secondary-electron-emitting surface, the electrons from which are directed into an electron multiplier. Pulses from both the electron and ion detectors are then time analyzed with a time-to-amplitude converter (TAC). In this way, an Auger event may be associated with a known scattering angle.

III. ENERGY ANALYSIS OF AUGER ELECTRONS

Figure 1 shows doubly differential measurements of electron production in Kr^{+}-Kr collisions plotted versus the electron energy for several collision energies. These noncoincidence, or singles, spectra are the result of counting all the electrons entering the electron spectrometer regardless of the collisions' impact parameter. Decay of the quasimolecule during the collision is responsible for most of the low-energy continuum extending from

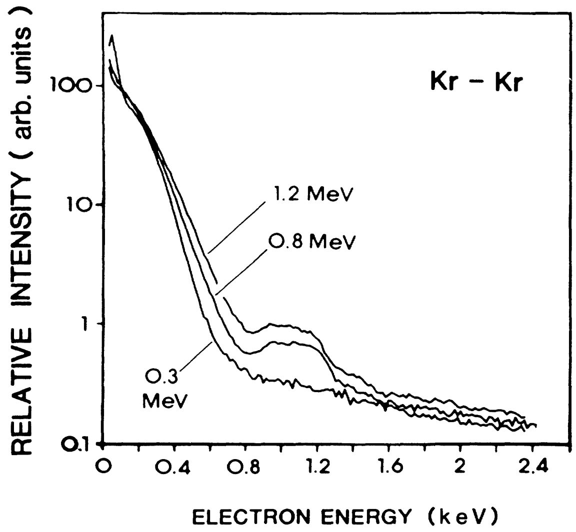

FIG. 1. Energy analysis of secondary-electron production in Kr-Kr collisions. The data sets have been corrected for the electron analyzer energy dispersion. The measurements are doubly differential—the controlled parameters are the electron energy (absissa) and the electron detector angle (fixed at 90°). The feature centered at 1100 eV is due to L Auger emission.

below 100 eV to about 800 eV (Refs. 2–6), while L Auger transitions are responsible for the broad peak at 1100 eV. It is interesting to note that since the life of the quasimolecule is on the order of 10^{-16}–10^{-17} sec, the ionizations taking place during the collision appear to occur much more rapidly than in isolated ions. Tokoro, Takenouchi, and Oda have observed rapid autoionization in He^{+}-He collisions which they attribute to a dynamic Auger effect, i.e., to the existence of a collision mechanism that increases the transition rate for these events.[8]

The spectra in Fig. 1 do not exhibit well-defined discrete structure, but the 1100-eV centroid of the L Auger peak indicates that we are not dealing with decay from singly ionized Kr. The 1100 eV-peak is almost 300 eV lower than the centroid of L-Auger spectra obtained by bombarding Kr with protons[9] or electrons.[10] Outer-shell ionization is responsible for shifting Auger energies in many atomic collision experiments[11,12] and it is important to consider this effect. We have calculated Auger electron energies for multiply ionized Kr (Ref. 13) and have found that the 1100-eV peak in Fig. 1 is attributable to L-vacancy decay in ions that are already 10–12 times ionized. These prior ionizations are a consequence of processes occurring during the collision.

The qualitative supposition that the Kr L Auger lines are superimposed upon a continuum background may be quantified by performing a background subtraction. This was done by fitting two exponentials to the background, one above and one below the L Auger region and subtracting their sum from the experimental curve.[14] The results of this procedure are shown in Fig. 2, where it is seen that the electron production rate from 900 to 1300 eV is strongly dependent upon the impact energy. Cleff,

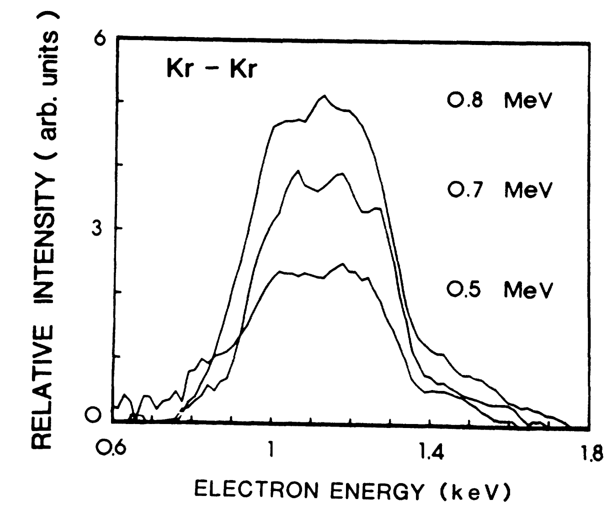

FIG. 2. Kr-Kr L-MM Auger electron-energy spectrum. The estimated background has been subtracted according to the procedure described in the text.

Woerlee, Shanker, and others have observed a similar energy dependence for L x-ray production.[15–19] Total L-shell x-ray and Auger electron-count rates as a function of collision energy are compared in Fig. 3. The total electron-count rates were obtained from the areas under corrected data curves, like those in Fig. 2. The Auger data have been arbitrarily normalized to the x-ray data in the plateau region to show the similarity in form of the

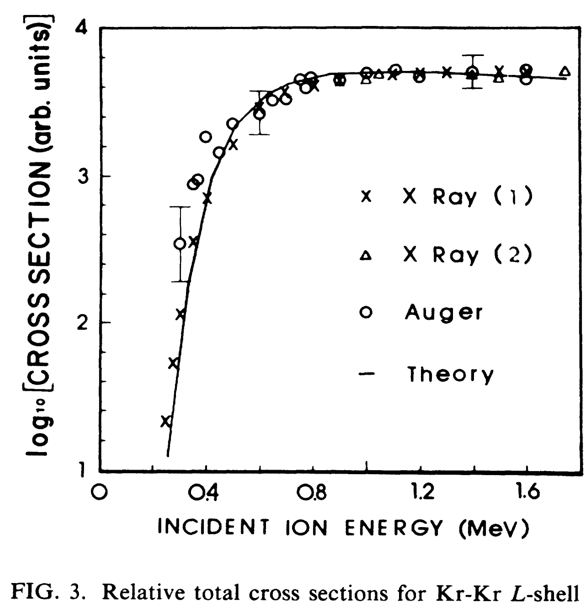

FIG. 3. Relative total cross sections for Kr-Kr L-shell phenomena. The Auger data are from the present work. The x-ray data sets 1 and 2 are from Refs. 17 and 19, respectively. The theory is from Ref. 19. The plots have been normalized to each other for comparison of functional dependency upon the collision energy. The error bars represent estimates of uncertainties in the subtraction of the backgrounds in Fig. 1.

impact-energy dependences of the relative total cross sections for the two modes of L-vacancy filling.

Shanker *et al.*[18,19] have proposed that rotational coupling of the $4f\sigma$ molecular orbital (MO) to the continuum via the $4f\pi$, $4f\delta$, and $4f\varphi$ orbitals of the Kr-Kr quasimolecule is responsible for the L-shell excitation in Kr-Kr collisions. Theoretical L-shell excitation total cross sections as a function of collision energy calculated by Shanker and coworkers are shown as the solid curve in Fig. 3. Provided that an overall normalization factor is used to correct for a difference in the theoretical and experimental absolute total cross sections, there is excellent agreement between the x-ray data and theory up to about 1.6 MeV. Above 1.6 MeV (not shown in the figure), the x-ray data and the rotational coupling calculations diverge and there is a factor-of-2 discrepancy at 3.2 MeV. Shanker and coworkers interpreted this discrepancy as indicative of another excitation mechanism: direct coupling of the $4f\sigma$ MO to continuum states, operating at small distances of closest approach. However, this *ad hoc,* qualitative assumption only partially compensates for the divergence of x-ray data and theoretical L-shell vacancy production. Further, no explanation has emerged as to the need for an overall normalization factor between the theoretical and experimental absolute cross sections. In the present paper it is suggested that changing fluorescence yields are the cause of the discrepancy between the data and their rotational coupling calculations.

IV. ION-AUGER ELECTRON COINCIDENCE EXPERIMENT

The present coincidence experiment associates an Auger event with a collision whose scattering angle is known. The electron-energy analyzer and detector, the scattered-ion detector, and the TAC are used to select those electrons that are ejected from collisions having a well-defined scattering angle, thus selecting a specific impact parameter. Figure 4 shows spectra for several incident ion energies obtained for a scattering angle of 10°.

In the 1.6- and 3.2-MeV data sets presented in Fig. 4, there are two reasonably well-resolved features separated by a consistently reproducible valley at 1.0 keV. There is also an indication of discrete structure in the broad peak from 1.0 to 1.3 keV. A rough comparison can be made of the data with what might be expected from Auger decay in an ion already having many vacancies in its outer shells. The theoretical lines in Fig. 5 indicate the energies and relative line intensities calculated by Chen and coworkers for relaxation of a Kr ion with a single vacancy in its L shell.[20] The solid curve shows these same data broadened by our apparatus function, corresponding to an overall instrumental resolution of 4%. Dirac-Fock calculations for Kr ions with multiple outer-shell vacancies have been carried out.[13] Each additional N-shell vacancy shifts the L-MM lines down in energy by approximately 20 eV and each additional M-shell vacancy shifts the L-MM lines down by approximately 35 eV. Although the experiment does not directly determine the

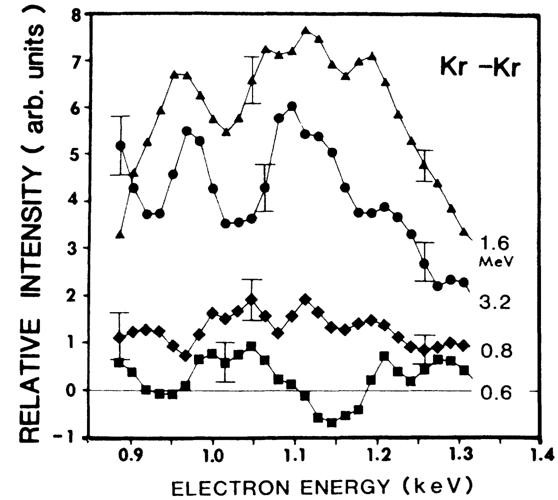

FIG. 4. Triply differential Kr-Kr L-MM Auger electron-energy spectra obtained with the ion-electron coincidence technique for collision energies from 0.6 to 3.2 MeV. The scattering angle is 10°.

final-charge state of the ion detected in coincidence with the electron, these shifts may be used to estimate the average charge of the ions at the time the Auger decay takes place. These calculations show that the 0.95-keV peak in Fig. 4 may be associated with $L_{2,3}$-$M_{2,3}M_{2,3}$ transitions from an ion that is already 12 (± 2) times ionized and which has a final-charge state of $+13$ after the Auger decay. The primary contribution to the two higher-lying peaks would then correspond to the $L_{2,3}$-$M_{2,3}M_{4,5}$ and $L_{2,3}$-$M_{4,5}M_{4,5}$ groups. However, the relative strengths of these groups are different from those shown in Fig. 5. A fit to the data can be obtained by as-

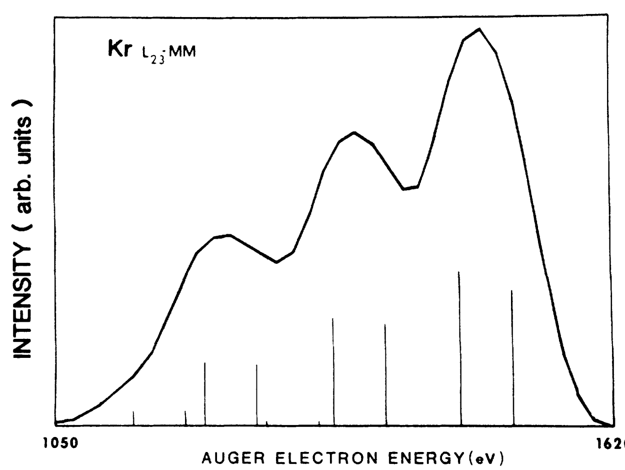

FIG. 5. The solid curve represents a computer simulation of the Kr^{+1} L Auger electron-energy spectrum that would be observed with the present instrumental resolution of 4%. The vertical lines represent the centroids and relative amplitudes of the 12 monoenergetic $L_{2,3}$-MM Kr^{+1} peaks calculated by Chen (Ref. 20).

suming, for example, three $M_{4,5}$ vacancies exist prior to the L-vacancy filling. We would expect from a statistical approximation that these vacancies would reduce the $M_{4,5}M_{4,5}$ line intensities by 50% and the $M_{2,3}M_{4,5}$ lines by 30%, relative to the Kr^{+1} values. The solid curve in Fig. 6 is a spectrum simulation based on these assumptions.

The reduction in relative intensity of the transition groups that involve the $M_{4,5}$ subshell point to a reduction in the occupation number of this level. This makes good physical sense, because fast, low-energy transitions between subshells would tend to transfer vacancies into the outer $3d$ orbitals. Thus the structure of the coincidence spectra gives us yet another verification of the proposition that multiple ionization of the outer shells occurs before the L shell is filled by an Auger (or x-ray) process. However, this simple statistical calculation of the Auger yields should not be taken as a demonstration that other electron configurations, including those involving $M_{2,3}$ ($3p$) vacancies, are not possible.

It should be noted that similarity in the 1.6- and 3.2-MeV data sets (cf. Fig. 4) shows that the charge state established before the L-vacancy decay is not sensitive to the distance of closest approach for this scattering angle and these collision energies. Evidently, most L vacancies are produced in those small-impact parameter collisions for which outer-shell processes remove a nearly constant number of electrons before the Auger decay can occur.

The data sets in Fig. 4 imply a threshold for L-shell excitation between 0.6 and 0.8 MeV, 10°; corresponding to a distance of closest approach of about 0.18 a.u. and an impact parameter of about 0.16 a.u. Figure 7 is a comparison of the integrated Auger count rates and the impact-parameter-dependent computations of Shanker and coworkers for $4f\sigma$ excitation. The impact parameter has been calculated from the scattering angle (10°) and the collision energy by assuming a Moliere potential. The data sets have been normalized to the rotational-coupling theory curve (theory 1). It appears that the electron data do not grossly deviate from the curve obtained from rotational-coupling calculations alone. Similar results were obtained for a 16° scattering angle. These data do not support the notion of a significant contribution from direct coupling of the $4f\sigma$ MO to continuum states, as proposed by Shanker *et al.* in order to explain the large x-ray cross sections at 3.2 MeV.

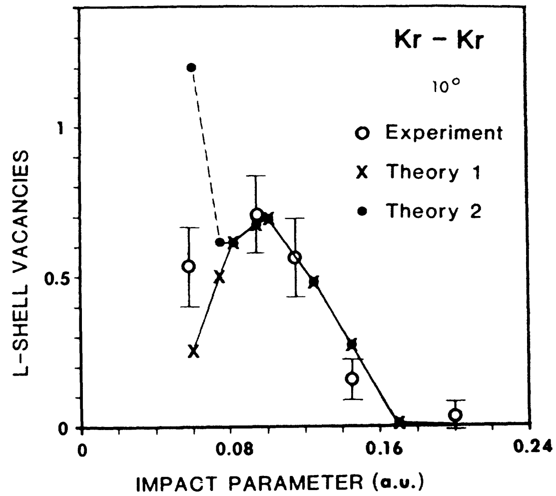

FIG. 7. Impact-parameter dependence of Kr-Kr L-shell phenomena. The experimental points represent the Auger data from the present work. The theory points are derived from $4f\sigma$ excitation calculations [Ref. (19)]. Theory 1 is for rotational coupling alone; theory 2 is for rotational coupling plus direct coupling to the continuum. The plots have been normalized to each other for comparison of functional form.

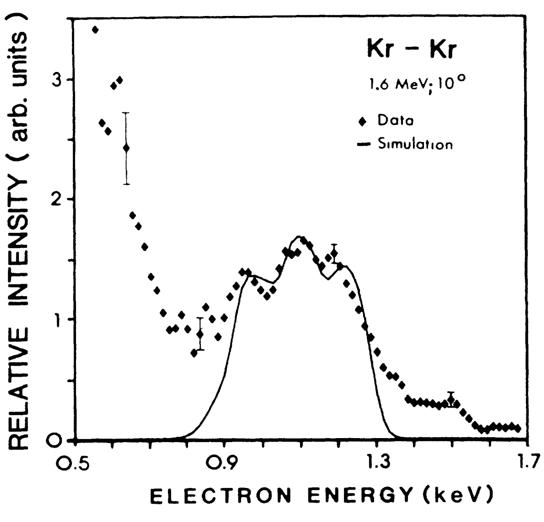

FIG. 6. Impact-parameter-dependent Kr-Kr L-MM Auger electron-energy spectra obtained with the ion-electron coincidence technique. The projectile-ion scattering angle is 10° and the collision energy is 1.6 MeV, corresponding to an impact parameter of 0.9 a.u. The data points represent the average of five spectra. The simulation spectrum is constructed of $L_{2,3}$-MM Gaussian peaks shifted in energy to correspond to a post-transition charge state of +13 and broadened by 4% to account for the instrumental resolution.

V. DISCUSSION AND CONCLUSIONS

It is clear from the previous two sections that the Auger electron probe provides important information regarding the MO model applied to heavy ion-atom collisions. The conclusions reached, based on an evaluation of the electron spectra, may be summarized as follows.

Charge state

The L-MM Auger electron energies are characteristic of highly-charged ions, indicating that a large number of electrons are lost before the filling of the L-shell vacancy. These prior ionizations are the source of the 100–800-eV continuum electrons which dominate the low-energy region of the electron spectrum. The charge state immediately after the collision (10^{-16} sec) is greater than +10.

In very heavy-collision systems such as Xe-Xe, it had earlier been presumed that inner-shell Auger effects spawn further outer-shell ionization in cascade, adding significantly to the final-charge state of the collision partners.[21] However, according to final-charge-state measurements by Antar and Kessel, the overall ionization due to all mechanisms in low-MeV Kr-Kr collisions is 12–13 for collisions in this range of impact parameters, and it appears that the L-shell decay in Kr contributes only marginally to the final-charge state.

Excitation mechanism

L-shell excitation is due to rotational coupling of the $4f\sigma$, $4f\pi$, $4f\delta$ and $4f\varphi$ orbitals of the Kr-Kr quasimolecule, as proposed by Shanker *et al.*[18,19] The Auger yields conform to rotational coupling calculations even at small-impact parameters, and direct coupling of the $4f\sigma$ to the continuum does not appear to be as significant as supposed by Shanker and co-workers.

Fluorescence yield

The hypothesis of constant Kr L fluorescence yield has been assumed by researchers in correlating x-ray data to vacancy production. This is in contrast to the work done on the Ar-Ar system, in which the functional difference in x-ray and Auger yields with respect to collision energy demonstrated that the fluorescence yield could vary by as much as an order of magnitude.[22] Fortner, Woerlee, and Saris[17] have noted the independence of the fluorescence yield with respect to collision energy for the Kr-Kr system and have proposed that the x-ray emission rates are independent of charge state for the collision parameters under consideration. In support of this, these researchers cited calculations performed in 1972 for the fluorescence yield of Cu as a function of ion charge for ground-state configurations.[23] Fortner *et al.* concluded that the Kr^{+1} value of 0.022 provided by Krauss[24] was appropriate to Kr-Kr L-shell decay, and other researchers have consistently followed this reasoning.[16–19] The adoption of the single-vacancy value is reasonable provided that the ionization is small and at the moment of L-shell vacancy decay, any M-shell vacancies are confined to the outer, $M_{4,5}$ subshell ($3d$ orbital). If this is indeed the case, up to six vacancies could be present in the M shell without affecting the fluorescence yield. Cleff,[15] Woerlee,[16,17] and Shanker[18,19] and co-workers have all based their interpretation of x-ray yields on the assumption that no $M_{2,3}$ ($3p$) vacancies are possible. However, if even just one electron is removed from the Kr $M_{2,3}$ subshell the fluorescence yield is changed by almost a factor of 2.

This paper presents strong evidence, based on energy shifts in the electron spectra and changes in relative transition rates, for high-charge states and multiple M-shell vacancies. These vacancies reduce the probability of Auger phenomena involving M-shell electrons, with a possible corresponding enhancement of L-MM fluorescence yields. It is here proposed that the fluorescence yield is in fact dependent upon the charge state of the Kr atoms in these experiments, but since the charge state is stable with respect to distance of closest approach, the fluorescence yield is approximately constant over the range of collision parameters relevant to L-shell excitation experiments. This model is consistent with the experimental results of both x-ray and electron spectroscopy.

VI. SUMMARY AND ACKNOWLEDGMENTS

The analysis of the electron spectra presented herein, based on the energy shifts in the electron spectra and the changes in relative transition rates, presents a collision picture in which most of the ionization (20–25 electrons) occurs during the collision and is followed by Auger decay that contributes relatively little (one charge state per ion) to the overall ionization. The high degree of ionization before the L-shell decay is fundamental to the determination of the sequence of ionization phenomena and to the interpretation of anomalous x-ray data observed by other researchers.

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