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J H D Eland^{1,2}, R J Squibb^{2,3}, M Mucke³, S Zagorodskikh^{2,3}, P Linusson⁴ and R Feifel^{2,3}¹ Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, UK² Department of Physics, University of Gothenburg, Origovägen 6B, SE-412 96 Gothenburg, Sweden³ Department of Physics and Astronomy, Uppsala University, Box 516, SE-751 20 Uppsala, Sweden⁴ Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, SwedenE-mail: raimund.feifel@physics.gu.se**Keywords:** collective Auger decay, multi-electron coincidence, inner shell vacancies**Abstract**

Using a multi-electron coincidence technique combined with synchrotron radiation we demonstrate the real existence of the elusive three-electron collective process in resonant Auger decay of Kr. The three-electron process is about 40 times weaker than the competing two-electron processes.

Introduction

In 1993, Lee *et al* proposed and gave some evidence for a new three-electron Auger transition, which followed the excitation of a pre-edge resonance in Kr [1]. Three-electron non-resonant Auger transitions had been suggested earlier [2], but clear evidence for just one such transition in Ar was found [3] with very low intensity relative to normal Auger. These unusual transitions start from the creation of a double vacancy in an inner shell, which is then filled simultaneously and coherently by two outer-shell electrons; all the released energy is passed to a third electron, which is emitted. Such inner-shell double vacancies are normally at energies above the minimum fourfold ionization energy and are filled by two separate successive two-electron Auger transitions involving four electrons in all. An analogous unusual process where a double vacancy is filled by two electrons and a single photon is emitted was already known [4], but no three-electron Auger process had been demonstrated at that time. More recently a three-electron Auger process was suggested as a possible explanation of an observed feature in a beam-foil excited C³⁺ ion [5], and a related process was more clearly predicted and observed in a rare-gas dimer [6, 7].

Using a multi-coincidence method with synchrotron light we now examine the proposed Kr transition directly and in detail, and show that the process indicated by Lee *et al* [1] does certainly take place, with a small but significant branching ratio. We suggest that similar transitions can also take place in a wide range of molecules where double vacancies are created in inner valence shells below the onset of fourfold ionization, particularly the inner valence shells of heteroatoms in organic compounds.

Experimental

Monochromatic light was supplied at beamline U49/2-PGM-1 of the BESSY II storage ring of the Helmholtz Zentrum Berlin, operating in single bunch mode, giving sub-nanosecond pulses at a repetition rate of 1.25 MHz. As the inter-pulse period of 800.5 ns at this rate is much shorter than most electron flight times, the rate was reduced to 78 kHz by a synchronous chopper [8]. Ionization was caused where the light intersected an effusive beam of Kr from a thin hollow needle and spectra of photoelectrons were recorded using a magnetic bottle time-of-flight electron spectrometer, which has been described before (see [9] and references therein). Briefly, the photoelectrons are constrained by the divergent magnetic field (ca. 0.8 T) of a conical permanent magnet and the weaker field of a long solenoid (ca. 10⁻³ T) to follow almost parallel trajectories to a 2 m distant microchannel

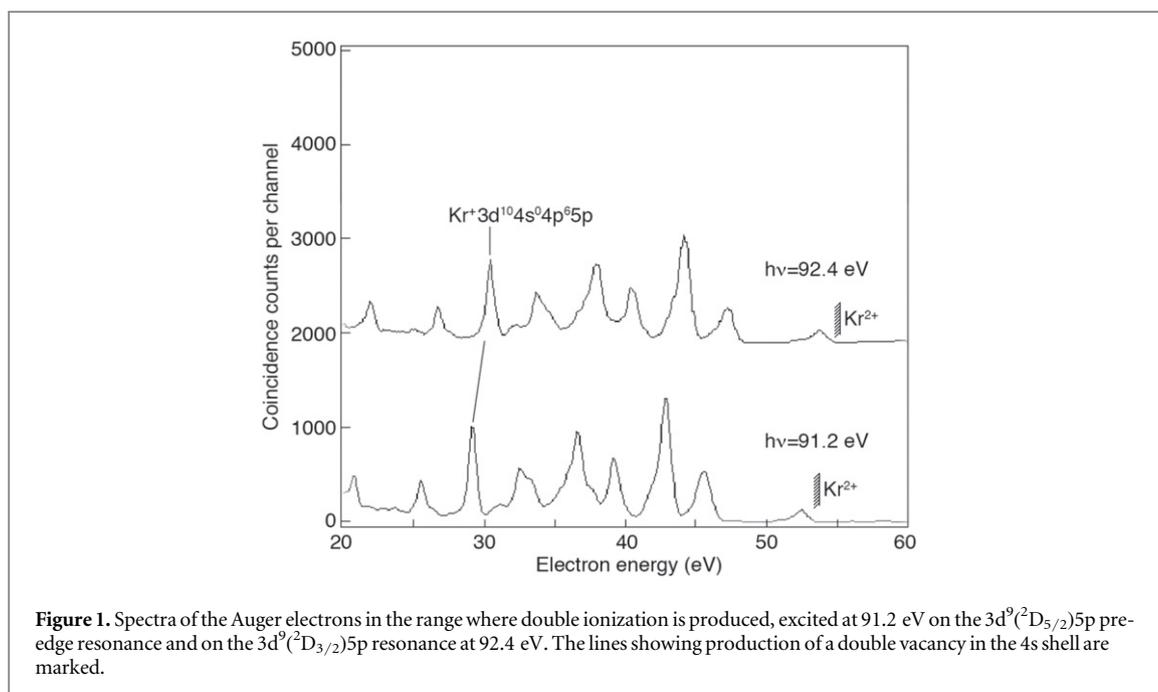


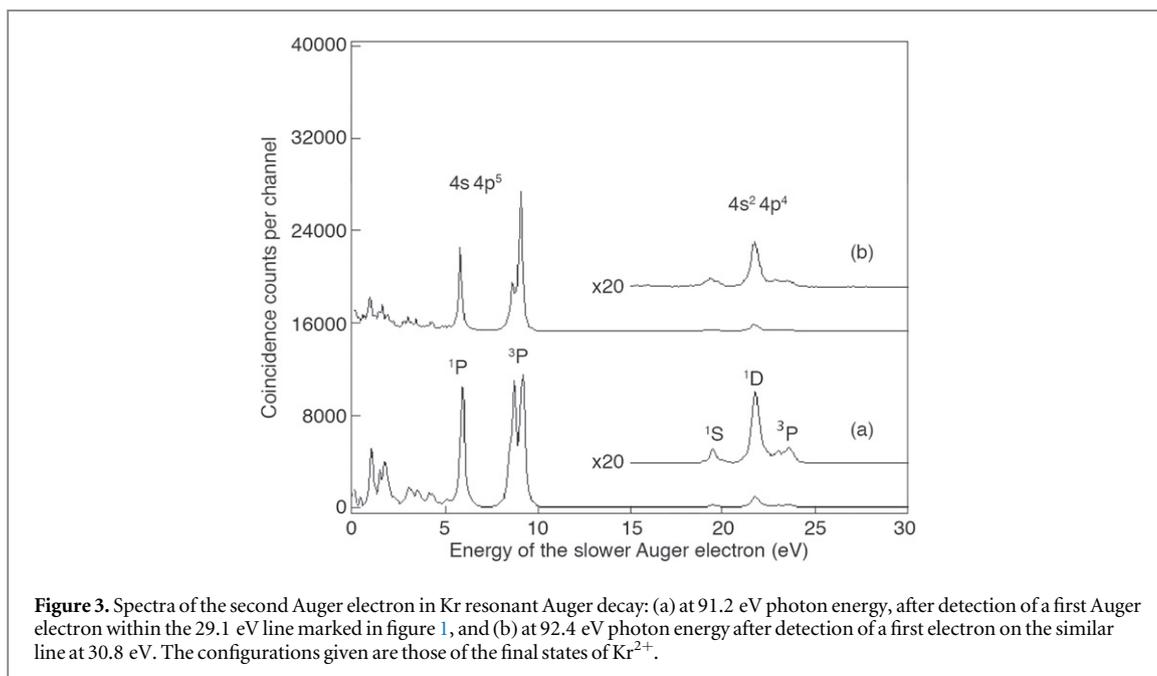
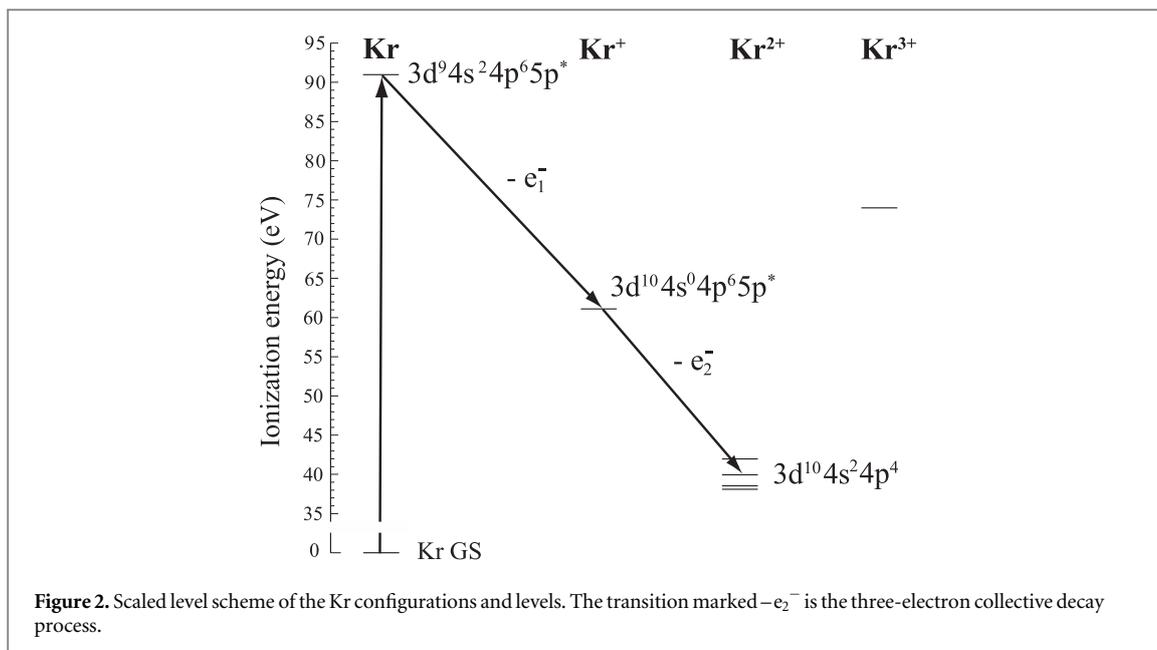
Figure 1. Spectra of the Auger electrons in the range where double ionization is produced, excited at 91.2 eV on the $3d^9(^2D_{5/2})5p$ pre-edge resonance and on the $3d^9(^2D_{3/2})5p$ resonance at 92.4 eV. The lines showing production of a double vacancy in the 4s shell are marked.

plate (MCP) detector. Individual electron arrival times relative to the light pulse time are registered by a multi-hit time-to-digital converter and are recoded using an on-line computer. As almost all (>90%) photoelectrons with energies below about 300 eV from a point source reach the detector, the overall collection plus detection efficiency is restricted mainly by the active area of the MCP, which is near 50%. The numerical energy resolving power $E/\Delta E$ was about 50 under the conditions of this experiment. The total electron count rate was kept to about 1000 s^{-1} to ensure that the rate of accidental coincidences was very small. The accidental coincidence pattern was calculated assuming a random distribution of events; its contribution to the true coincidence signal of interest in this study was found to be negligible.

Results

The transition identified by Lee *et al* [1] starts with the absorption of a 91.2 eV photon to excite the system to the $3d^9(^2D_{5/2})5p^*$ pre-edge resonance in Kr. The major relaxation pathway from this resonance is Auger decay, producing singly, doubly and triply charged Kr ions; the fractions of each, as known from the ion yields [10] are 5% Kr^+ , 88% Kr^{2+} and 7% Kr^{3+} . The complete resonance Auger electron spectrum containing all these contributions is highly structured and has been studied in some detail before [11]. Almost all the structure, except for the part attributed to Kr^+ formation, represents excited Kr^{+*} states which later autoionize, mainly to Kr^{2+} . From the electron–electron coincidence signals we can extract the part of the resonance Auger spectrum which leads to double ionization, excluding the Kr^+ and Kr^{3+} contributions; the spectrum is shown in the lower part of figure 1. In addition to the prominent structure, it includes a weak continuum, which is due to direct double Auger decay where two outgoing electrons share the excess energy as a smooth distribution.

In figure 1, the line at 29.1 eV electron energy singled out by Lee *et al* [1] is marked. The line is firmly attributed to a state of Kr^+ at 62.1 eV binding energy, with the dominant configuration $3d^{10}4s^04p^65p$, that is, with a double vacancy in the inner-valence 4s shell [12, 13]. This state is at lower energy than both the triple and fourfold ionization energies of Kr and so can decay non-radiatively only to Kr^{2+} . Decay from this double vacancy state to the states of the lowest energy configuration of Kr^{2+} , namely $3d^{10}4s^24p^4$, can occur only by a three-electron transition in which two electrons fill the vacant orbital and one electron is ejected, as illustrated in figure 2. But the low energy states of Kr^{2+} are also populated by direct double Auger decay, which produces the continuum underlying the sharp Auger line. This continuum could not be subtracted or allowed for in interpreting the overall Auger spectrum used by Lee *et al* [1], which is an amalgamation of all the many processes happening after excitation. So to test whether three-electron decay really occurs we first extracted the spectrum of the second electron from double Auger in coincidence with the 29.1 eV Auger line, so obtaining a spectrum from this specific decay alone, shown in figure 3(a). To determine whether the apparent population of the Kr^{2+} ground configuration is due to the proposed process or to the underlying continuum we extracted an equivalent spectrum coincident with a section of the spectrum of equal width on the low energy side of the line, due mainly to the continuum. The two spectra were then put on a common double ionization energy scale by including the



29.1 eV line, for comparison and direct subtraction. As expected, the continuum populates the Kr^{2+} ground state, but with only a third of the intensity seen in the indirect Auger decay. The form of the spectrum is not significantly changed by subtraction.

The group of lines representing the ground state configuration of Kr^{2+} and shown in figure 3 is definitely produced by the three-electron decay but is overwhelmed in intensity by emission of lower energy electrons, forming highly excited Kr^{2+} states in the range of 52–56 eV. The major lines are readily identified as levels from the configuration $3d^{10}4s^14p^5$. Since this configuration can be reached from the intermediate double vacancy state by a two-electron transition, it is not surprising that branching to it is much stronger than branching to the ground state configuration. After subtraction of the continuum background, the total signal for the three-electron channel is 1/40 of the two-electron signals. To take the investigation slightly further, we used excitation of the higher energy ($J = 3/2$) spin-orbit component of $3d^9(^2D)$ creating a pre-edge resonance with configuration $3d^9(^2D_{3/2})5p^*$ at 92.4 eV. The same double vacancy configuration as before is then reached by emission of an Auger electron on the line at 30.7 eV electron energy, as illustrated in figure 1 (upper spectrum); the second Auger electron spectrum in coincidence with this line is shown in figure 3(b). The same final states are formed with about the same intensity relative to the two-electron products, but some branching ratios to specific

final states are subtly different, probably reflecting different relative populations of the unresolved $3d^{10}4s^04p^65p$ ($^2P_{3/2,1/2}$) levels. There may also be some contribution by the configuration $3d^9(^2D_{5/2})6p^*$ in the absorption line at 92.4 eV, but the near-identity of the spectra suggests that this is a minor component. The relative importance of this and other possible contributing pathways could be estimated only by theory, which is at present a practically intractable task.

Conclusions

To summarize, the three-electron process put forward by Lee *et al* [1] is clearly shown to exist, with a branching ratio only weaker by a factor of 40 than competing two-electron processes populating more highly excited states of the dication. Its relative strength in the face of such competition is perhaps surprising. Lee *et al* [1] point out, following von Raven *et al* [13], that there are other processes involving four-electron transitions, which could contribute, but we agree with them that such processes are unlikely to be of sufficient intensity to invalidate this conclusion. As this three-electron Auger decay is real, we can expect similar processes in other cases. Double vacancies in 1s inner shells of first-row atoms are always far above the fourfold ionization energies, but this is not true of double vacancies in inner valence orbitals, which often lie below them, like the double vacancy state in Kr demonstrated here. Where such double inner-valence vacancy states of doubly charged ions lie below the fourfold ionization threshold but above the triple ionization threshold of a molecule, three-electron Auger decay may be a favorable relaxation pathway. Formation of the double vacancy is then a two-electron process whereas the competing direct triple ionization involves three electrons. This situation is unlikely to arise in compounds of carbon and hydrogen only, but must be fairly common where heteroatoms of nitrogen, oxygen or fluorine are present.

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