$M_{2,3}$-Region X-Ray Emission Spectrum from Gaseous Krypton

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The $M_{2,3}$ x-ray emission spectrum of gaseous krypton excited by direct electron bombardment has been recorded with a scanning single-flat crystal spectrometer. The most prominent spectral features are two peaks at 187 and 203 eV, with the 187-eV peak having an extended low-energy tail. This low-energy tail is attributed to double-electron single-vacancy transitions owing to the strong mixing of the final-state configuration $4s4p^6\,{}^2S$ with the even levels $4s^24p^4ns\ {}^2S$ and $4s^24p^4nd\ {}^2S$. The 203-eV peak is identified as probably the single-electron double-vacancy $M_{2,3}M_{2,3} \to M_{2,3}N_1$ multiplet complex.

$L_{2,3}$ x-ray emission spectra[1] from Ar and KCl were measured and were found to have a low-energy satellite which was interpreted as evidence of a semi-Auger (double-electron) process. The separation[2] of the L_2 and L_3 levels of only 2 eV and the limited resolution of the spectrometer did not permit a more detailed display of the line structure. Recently, a high-resolution $L_{2,3}$ emission spectrum[3] of gaseous Ar has been reported which showed the line structure.

To investigate this semi-Auger process further with the limited resolving power at hand, it would be very desirable to choose a system with a larger spin-orbit splitting than Ar $L_{2,3}$ to reduce overlapping of individual lines. Since the energy separation of the inner subshells increases with atomic number, the next-heavier monatomic gas, krypton, would be a promising atomic system. The krypton $M_{2,3}$ emission with a spin-orbit splitting[4] of the M_2 and M_3 levels of about 8 eV would be analogous to the Ar $L_{2,3}$ emission spectrum. Also, krypton would provide an opportunity to observe this process as a function of atomic number.

The $M_{2,3}$ emission spectrum from gaseous krypton of research grade was obtained on a single-flat-crystal spectrometer with photon counting. An electron beam emanating from an electron gun operating at 10 kV and 100 mA excited the spectrum by direct bombardment of the gas effusing from a conventional slit nozzle. The radiation was dispersed with a lead myristate Langmuir-Blodgett-type crystal. The energy scale of the spectrum was anchored to the Mo $M\zeta$ ($M_{4,5} \to N_{2,3}$) line[5] at 63.476 Å (129.29 eV). For further discussion of the experimental apparatus, the reader is referred elsewhere.[6]

In Fig. 1 is shown the x-ray emission spectrum in the $M_{2,3}$ region of gaseous krypton. This spec-

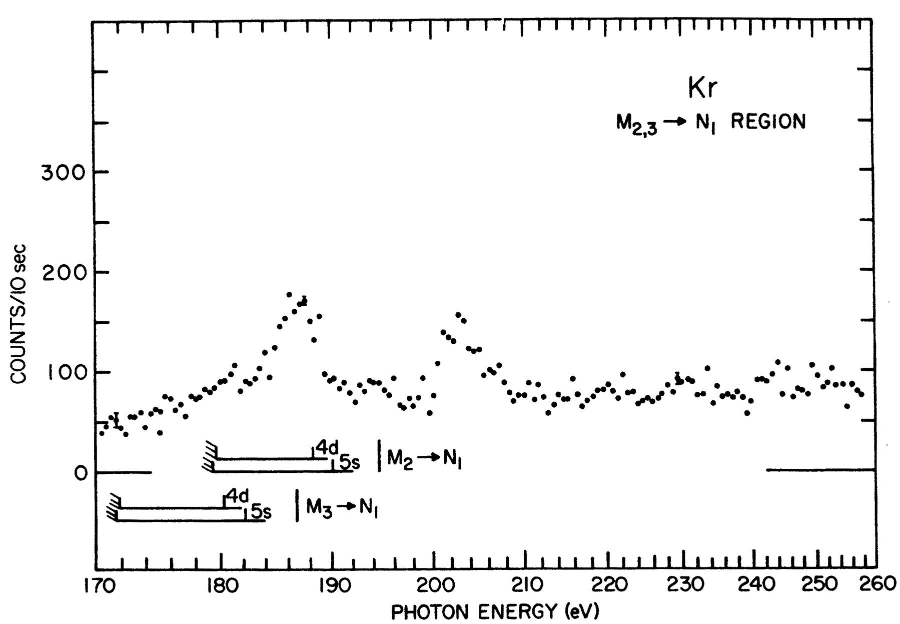

FIG. 1. X-ray emission spectrum from gaseous krypton in the $M_{2,3} \to N_1$ region. Beneath the spectrum are plotted the positions and limits of the ${}^2S$ levels taken from Refs. 7 and 9. The bars at about 172, 188, and 230 eV indicate the percentage statistical deviation of the data.

trum is the average of two scans with a 10-sec-per-point dwell time. A similar profile was obtained several months before the accumulation of the data in Fig. 1. An inadequate supply of krypton gas at the time of this measurement and the later dismantling of the apparatus to set up a different experiment cut short the ability to obtain more data. The prominent features of the spectrum are two peaks of comparable intensity separated by about 16 eV with the low-energy side of the 187-eV peak tailing off. In view of the limitation due to the poor signal-to-noise ratio only the gross features will be discussed.

We know from recent determinations that the energies required to form single vacancies in the M_2, M_3, and N_1 subshells are 222.2, 214.4, and 27.4 eV, respectively.[4] The single-electron single-vacancy transitions $M_{2,3} \rightarrow N_1$ should occur then at photon energies of 194.8 and 187.0 eV. Thus, the prominent peak at about 187 eV in Fig. 1 is identified as the $M_3 \rightarrow N_1$ transition and the bump at about 195 eV is the $M_2 \rightarrow N_1$ transition. The departure from the expected intensity ratio of 2 to 1 for $M_3 \rightarrow N_1$ to $M_2 \rightarrow N_1$ can be taken as an indication of an appreciable difference in the decay rate of the initial states by other nonradiative processes, i.e., Auger and/or Coster-Kronig transitions. This unexpected intensity ratio could also be due to double-vacancy transitions, as discussed below.

The extended tail on the low-energy side of the 187-eV peak is attributed to double-electron transitions resulting from the strong mixing of the final-state configuration $4s4p^6\,{}^2S$ with the even levels $4s^24p^4ns\,{}^2S$ and $4s^24p^4nd\,{}^2S$. The analysis of Kr II spectra by Minnhagen[7] indicated that $4s4p^6\,{}^2S$ mixes strongly with $4s^24p^4nd\,{}^2S$ and weakly with $4s^24p^4ns\,{}^2S$. Reader and Epstein[8] came to a similar conclusion in their analysis of the spectra of Rb III, which is isoelectronic with Kr II. Thus, the main contributions will be from the strong mixing of $4s4p^6\,{}^2S$ and the $4s^24p^4nd\,{}^2S$ configurations. Plotted in Fig. 1 are the positions[7,9] of the ${}^2S$ levels relative to the $4s4p^6\,{}^2S$. The insufficient resolution does not permit a complete comparison of the positions of the *ns* and *nd* levels.

The peak centered at about 203 eV is identified as a high-energy satellite multiplet complex to the parent $M_{2,3} \rightarrow N_1$ transitions. A number of possible radiative single-electron double-vacancy dipole transitions are listed[10] in Table I. Observe that both the $M_{2,3}M_{2,3} \rightarrow M_{2,3}N_1$ and $M_{2,3}N_1 \rightarrow N_1N_1$ transitions can occur in the region of the 203-eV peak. However, it is unlikely that both these radiative transitions would occur in the same atom as a cascade. The $M_{2,3}N_{2,3} \rightarrow N_1N_{2,3}$ could make a contribution in the 187-eV-peak region that may possibly account for its large intensity relative to the 195-eV bump. The 215-eV region does not appear to contain any change of emission intensity that could be attributed to the $M_{2,3}M_{4,5} \rightarrow M_{4,5}N_1$ transition.

TABLE I. Some possible single-electron double-vacancy transitions (Ref. 10) of gaseous krypton.

$M_{2,3}M_{2,3} \rightarrow M_{2,3}N_1$	204.6 eV
$M_{2,3}M_{4,5} \rightarrow M_{4,5}N_1$	215 eV
$M_{2,3}N_1 \rightarrow N_1N_1$	201 eV
$M_{2,3}N_{2,3} \rightarrow N_1N_{2,3}$	179–189 eV

A comparison of the emission intensity of the 187- and 203-eV peaks suggests a comparable probability of producing the single-vacancy $M_{2,3}$ and double-vacancy states under these experimental conditions. This is not at all unexpected. The $M_{2,3}$ single-vacancy states are produced solely by an initial collision of the incident bombarding electron with the neutral krypton atom. Production of double-vacancy states by shake off would be on the order of up to 10% of the initial single vacancies. In addition, double-vacancy states can be produced as the final states of nonradiative processes,[11] i.e., Auger and Coster-Kronig. Thus, on the basis of the known relatively large probability of the Auger transitions $L_{2,3} \rightarrow M_{2,3}M_{2,3}$ and the coincidence of the expected and experimental peak-energy position, the 203-eV peak is identified as the $M_{2,3}M_{2,3} \rightarrow M_{2,3}N_1$ multiplet complex.

The weak lesser structure above 220 eV is probably due to single-electron triple-vacancy transitions. The transitions[12] $L_{2,3} \rightarrow L_1$ can occur at 196 and 249 eV, respectively, but the very rapid decay of the L_1 single vacancies by Auger and/or Coster-Kronig transitions makes observations of the radiative $L_{2,3} \rightarrow L_1$ transition very unlikely.

In conclusion, $M_{2,3}$ x-ray emission spectrum from gaseous krypton, excited by electron impact, has been shown to contain contributions from a semi-Auger (double-electron) process. Unanticipated results of this work were the measurement of comparable intensities for the identified double-vacancy transition $M_{2,3}M_{2,3} \rightarrow M_{2,3}N_1$ and the single-vacancy transitions $M_{2,3} \rightarrow N_1$, and the large departure from 2 to 1 of the relative intensity of the assigned $M_3 \rightarrow N_1$ and $M_2 \rightarrow N_1$ transitions.

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[10]The binding energies of $M_{2,3}M_{2,3}$ and $M_{2,3}M_{4,5}$, 468.6 and 351.0 eV, respectively, were obtained from the *L-MM* Auger spectrum (Ref. 4). $M_{2,3}N_{2,3}$, 235.2–242.2 eV; $M_{4,5}N_1$, 136 eV; and $N_1N_{2,3}$, 52.8–56 eV were obtained from the *M*-shell Auger and Coster-Kronig study [W. Mehlhorn, Z. Phys. **187**, 21 (1965)]. $M_{2,3}N_1$, 264 eV, was obtained from the energy loss in coincidence with ions-formed study [Th. El-Sherbini and M. J. Van der Wiel, Physica (Utr.) **62**, 119 (1972)]. This tentative value is in good agreement with the binding energy for $M_{2,3}N_1$ of 262.5 eV determined by taking the difference of the calculated total energy between Kr and $Kr^{+2}(3p)(4s)$ that was computed with the Froese-Fisher H-F program. A value of 62.9 eV was obtained for N_1N_1 (Ref. 9).

[11]It is also possible to ascribe the similar emission peak intensities as due largely to differences in decay rates of the single- versus double-vacancy states. There is not enough information at hand to detail such an argument.

[12]The single-vacancy L-shell binding energies were obtained from Ref. 4.