Energy Distribution of Electrons from Ionizing Collisions of Atoms and Ions*

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The energy distribution of electrons ejected in collisions of Ne ions with Ne and He atoms, He ions in Ne, and Kr, and Xe ions and neutral atoms in Kr and Xe, respectively, have been measured for ion energies from 0.3 to 3.0 keV. The spectra consist of a continuous distribution decreasing monotonically with electron energy, on which there are superimposed electron groups of definite energy characteristic of the colliding particles. The nature and origin of these groups are discussed.

INTRODUCTION

MEASUREMENTS of the energy distribution of electrons ejected in ionizing collisions of ions and atoms, previously reported[1] for argon ions and neutral atoms in argon and for helium ions and neutral atoms in helium, have been extended to neon, krypton, and xenon. Definite evidence has been found which indicates the formation of intermediate excited states in the ionization process. These states seem to be quite limited in number even for heavy atoms and are of sufficient energy to eject electrons with kinetic energies of the order of 10 eV. The experimental technique was described in detail in the initial report and so is only summarized here.

Ions produced in a source by electron bombardment are focused and selected by a low resolution mass spectrograph, neutralized by charge exchange if the corresponding neutral atom beam is desired, and then undergo collisions with a target gas in a field free region within a cylindrical fine wire grid. Electrons ejected in an ionizing collision arise at a point in space at which the electric potential can be varied relative to the metal electrodes of the region. This allows a definite separation of the electrons ejected from surfaces by ion or atom bombardment and those originating in ionizing collisions. Those electrons ejected in a narrow angular range are energy analyzed by a cylindrical condenser. This current is amplified by a secondary electron multiplier and an electrometer, and subsequently recorded.

A method of calibration of the analyzer system has been added for these measurements in which known potential differences introduced between the ionization cylinder and the analyzer produce definite shifts of the spectrum. Analysis of these measurements gave a calibration consistent within 1%; however, inaccuracies in measurement of the record charts, as well as fluctuations in space charge in the ionization region, raise the estimated error in the measurement of the absolute electron energy to about 2%.

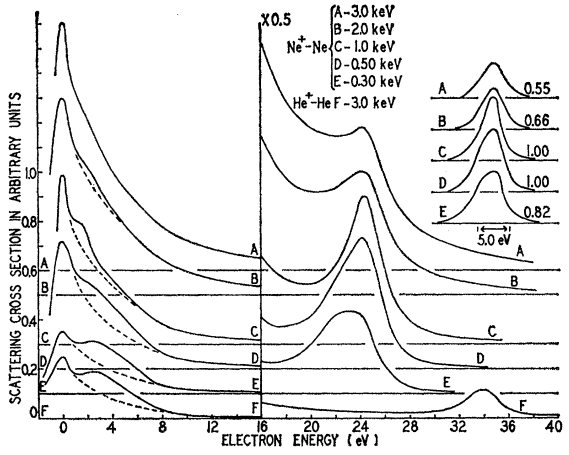

FIG. 1. Electron-energy distribution for ionizing collisions of Ne^+ in Ne, and (curve F) for He^+ in He. The ordinate scale for curve F is unrelated to the others. The relative net yields of the characteristic group for Ne^+–Ne are shown in the upper right-hand corner. The values given in keV for each curve represent the ion energy in the laboratory system.

MEASUREMENTS AND DISCUSSION

The electron energy distributions obtained so far for ionizing collisions of rare gas ions and atoms show a general similarity. Each seems to be composed of two distinct parts; one is a continuous spectrum which has its largest value at the zero of electron kinetic energy, and the second is composed of a number of electron groups of a limited energy range, which in yield and in energy are characteristic of the colliding particles. The

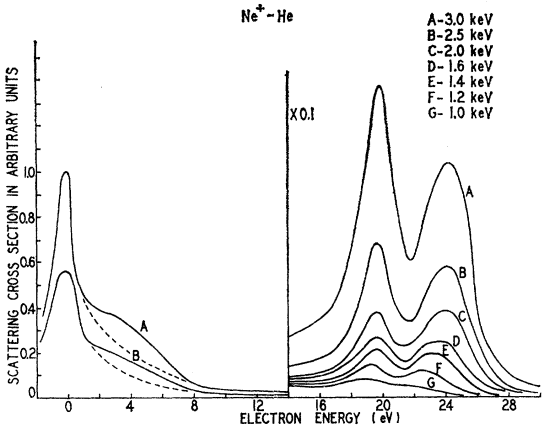

FIG. 2. Electron-energy distributions for ionizing collisions of Ne^+ in He.

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[1] H. W. Berry, Phys. Rev. **121**, 1714 (1961).

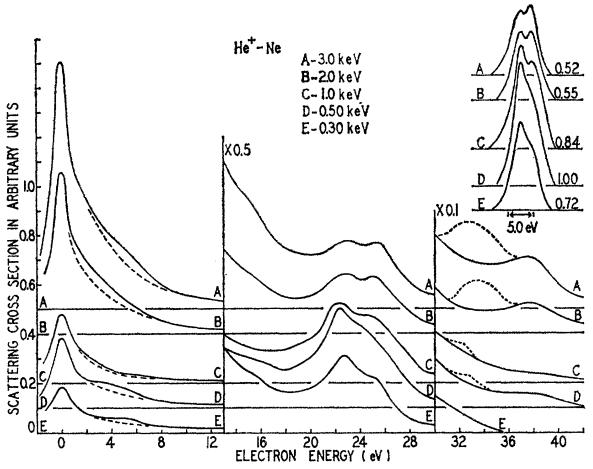

FIG. 3. Electron-energy distributions for ionizing collisions of He^+–Ne. The relative net yields are shown in the upper right-hand corner.

relative contribution of the two parts varies widely with the particles involved and the collision energy in the center-of-mass system.

Figures 1–5 show a number of observed electron spectra for various neon and helium combinations, for krypton ions and neutral atoms in krypton, and for xenon ions and neutral atoms in xenon. In Figs. 1–3, the ordinate is the observed electron current reduced to unit ion beam current and unit pressure. The data have also been corrected for the variation in slit width with electron energy. In Figs. 4 and 5, the yields are represented as a fraction of the value at zero electron kinetic energy, since no measurements were made of the equivalent atom current. The energies shown in keV for the various curves are the ion beam energies in the laboratory system. The peaks at 4 eV represent electrons from the grid wires and so should be disregarded.[1] In all cases, the continuous spectrum yield increases with increasing collision energy. However, the characteristic groups show both increasing and decreasing yields with ion energy. In Figs. 1 and 3 these groups are also shown with the continuous spectrum removed. For this comparison, the groups have been shifted along the abscissa so that the peaks are at the same point. The scale unit here is indicated by the arrow. It should be noted that the estimated linewidth produced by the size of the entrance and exit slits along with the effects of misalignment is about 3 eV in the region of 25-eV electron energy. Therefore, most of the width shown by the groups in Ne^+–Ne and Ne^+–He at the higher collision energies arises from the apparatus.

The energies of the characteristic groups observed are compatible with those that would arise from a process in which a double excitation of one of the particles occurs and is followed by autoionization. For example, the one group observed for He^+–He (Fig. 1)[2] occurs at 33.9 ± 0.5 eV, and thus, could result from the autoionization of a doubly excited state of 58.5-eV energy with the ionization potential of He taken as 24.6 eV. This is close to those calculated by Bransden and Dalgarno[3] for He $(2s2p)\ ^1P$, viz., 61.2 eV, or $(2s^2)\ ^1S$–59.4 eV. Double excitations of He by electrons have recently been observed by Lassettre and Silverman[4] in which they found an energy loss of 60.0 ± 0.1 eV in the forward scattering of 500-eV electrons. This has been attributed to the excitation of the $2s2p$ state. Quite possibly, the autoionizing state observed for He^+–He ionizing collisions is the same state found by Lassettre and Silverman though the difference in the observed energies is believed to be more than the experimental error. Up to 3.0 keV, the highest ion energy used, no other groups were observed for He^+–He though a yield of less than one-tenth that for the 34 eV line was measurable for electron energies up to 55 eV.

While there do not seem to be any calculations of doubly excited states in Ne or Ne^+ or any measurements which extend to the range of energies desired, an estimate of such states may be made following Herzberg.[5] Approximately, the energy of a doubly excited state

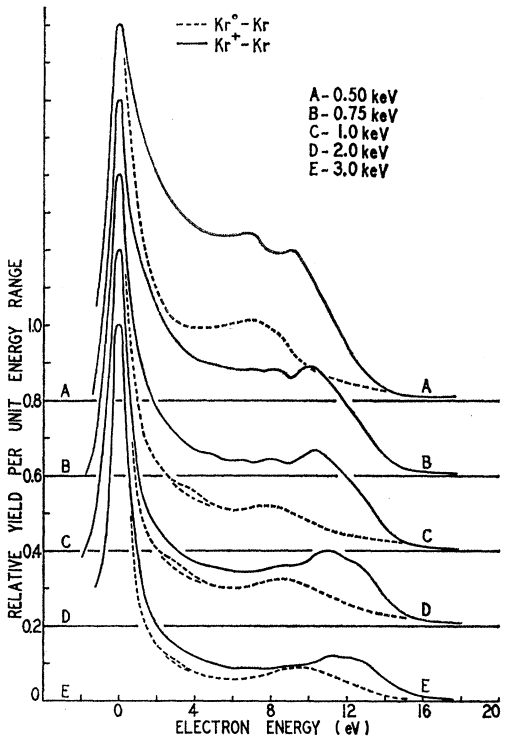

FIG. 4. Electron-energy distributions for Kr ions and neutral atoms in Kr. These are compared on a relative basis in which the yield at zero electron energy is taken as 1.0.

[2] A more accurate calibration of the energy analyzer has produced the difference in the abscissa scale for the He^+-He shown here and in the earlier report.

[3] B. H. Bransden and A. Dalgarno, Proc. Phys. Soc. (London) **A66**, 904 (1953).

[4] Reported by U. Fano, Phys. Rev. **124**, 1866 (1961).

[5] G. Herzberg, *Atomic Spectra and Atomic Structure*, (Dover Publications, Inc., New York 1944) p. 167.

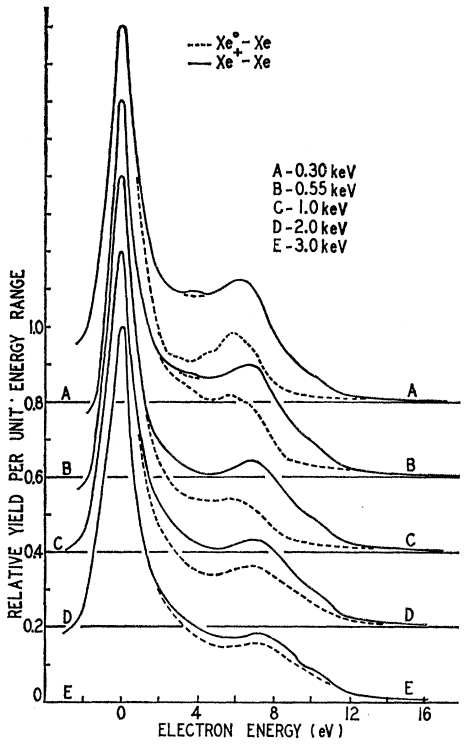

FIG. 5. Electron-energy distributions for Xe ions and neutral atoms in Xe. These are compared on a relative basis in which the yield at zero electron energy is taken as 1.0.

can be found by adding to the energy of a single excitation that of the second excitation taken as the value belonging to the ion. The justification for this lies in the reasonable assumption that the first excitation will affect about equally the initial and final states of the second excitation. Hence, the energy would be about that for the same transition in the ion. If this is done for Ne^+–Ne, there are a large number of excited states which will produce electrons of the energy of the single observed group. However, the width and behavior of the group point to the autoionization of a single state as the source.

Bates and Massey[6] have discussed in general terms the expected behavior of a cross section for a process such as this. They consider the probability of a transition occurring at the intersection of the potential curves representing the initial and final states of the pseudomolecule produced in the collision. Their analysis indicates that, approximately, the cross section should vary inversely as the relative velocity of the motion, if sufficient energy is available for the crossing to occur. In the collision range studied, the 24-eV characteristic group in Ne^+–Ne shows an increase with relative velocity followed by a rather broad maximum, and then a decrease which goes very nearly as the reciprocal of the relative velocity. A similar behavior is shown also for the two unseparated groups in He^+–Ne (Fig. 3). For He^+–He and for Ne^+–He, the net yield increases with increasing energy in the range observed. The width at half height (Ne^+–Ne) decreases from about 5 eV at 0.3 keV to 4 eV at 1.0 keV and then remains essentially constant. This limit is largely instrumental.

In Ne^+–He, two well-defined groups are produced (see Fig. 2). Here, the low-energy end of these spectra is shown only for the two highest ion energies. A like behavior, but smaller and less reliable in this region because of the large background, occurs for the other ion energies. The increasing sharpness of the groups with collision energy would indicate that they are produced by autoionization of one of the particles rather than of the temporary molecule formed in the collision. No energy states of doubly excited He could produce electrons of these energies in an autoionization process, and so these must be the result of autoionization of neutral or ionized neon. However, the peak shift with relative velocity shown in the spectra would indicate that it is the autoionization of neutral neon. This is discussed below. For collision energies less than 1.0 keV, the autoionization process is undetectable above the background which is produced by ionizing collisions of the Ne-ion beam with the Ne gas which has diffused into this region from the source.

An upward shift of the energy of the characteristic groups with increasing collision energy occurs for most ionizations produced by ions. While this shift, in some cases, is little more than the experimental error in the energy of the electron group, for the 24 eV line in Ne^+–He, it is relatively large and quite readily measured because of the well-defined peaks. Measurements made directly on the recorder charts showed that the peak shifts outward as $E_0^{-\frac{1}{2}}$, where E_0 is the ion energy. A similar but less marked shift occurs for the Ne^+–He peak at 19 eV. If one assumes that the doubly excited state undergoes an exponential decay with lifetime τ, the electron will be ejected in the attractive field of the neighboring ion (He^+) at varying distances from the crossing point at which the excitation is assumed to occur. With the assumption that the crossing point is not a function of the relative velocity, and further is small compared to the separation at ejection, a simple dependence of the electron energy displacement from the value at infinite separation from the ion can be obtained. The line shape is given by

$$(A/E_0^{\frac{1}{2}}V^2\tau)\exp(-b/V\tau E_0^{\frac{1}{2}}),$$

where A and b are constants and V is the energy displacement. From the line maximum shift with relative velocity, a rough value of τ can be obtained. For the 24-eV Ne^+–He group, this is about 2×10^{-15} sec. Also, the linewidth at half maximum depends on τ, but the true width is obscured here by the apparatus width. A width of 4 eV, though, would be consistent with this value of τ. For the 19-eV group, the shift is less reliably measured but the indicated lifetime is about 4×10^{-15}

[6] D. R. Bates and H. S. W. Massey, Phil. Mag. 45, 111 (1954).

sec. The energy of the groups at infinite separation is found by extrapolation to be 21.2 and 27.4 eV.

Values for the lifetimes of doubly excited states against autoionization have been calculated for He by Wu[7] and by Bransden and Dalgarno,[3] but no calculations seem to be available for the other rare gases. The values found for He range from about 1×10^{-15} to 2×10^{-14} sec. At the relative velocities of motion here, the mean internuclear separation at ejection would range from several to ten angstroms. At these close distances, one might expect the electric field of the ion to produce a sizeable Stark displacement of the energy levels. This may be the explanation of the peak shift for Ne^+–Ne which varies approximately as $1/E_0^2$.

Three distinct groups are observed for He^+–Ne, at 22.5, 25.5, and 38 eV. See Fig. 3. The dashed peak at 34 eV is the result of an incomplete subtraction of the background He^+–He. Examination of the recorder charts indicates that this peak is identical with that which appears on the background gas run. Compared with the 38-eV peak, the yield is quite large, and since the correction for this involves an unknown adjustment for the effect of the addition of neon gas on the ion beam, this background contribution is not always wholly removed. For other parts of the spectrum the error incurred is unimportant. The groups at 22.5 and 25.5 eV are too close to determine the line shift with the present resolution. Very likely, these represent an autoionization of Ne. The 38-eV group could arise from either He or Ne, but the autoionizing state (62.6 eV) is nearly at the same value as one of the energy losses observed by Lassettre and Silverman[4] (63.5 eV) for electrons in He. A characteristic group near 25 eV occurs for all cases involving Ne. It would seem reasonable to ascribe these to the same autoionization process except that the line shift with relative velocity is not the same for all. This is particularly apparent in comparing the Ne^+–He data records with the background gas (Ne^+–Ne) runs taken at the same time.

The electron distributions for Ne^0–Ne have also been measured and are unusual in that they are almost entirely composed of the continuous spectrum. Only at low collision energies is there just a trace of a group at 14 eV. The distributions are nearly logarithmic with a negative slope (on a semilogarithmic plot) which decreases in absolute value with the collision energy, E_0 approximately as $E_0^{-\frac{1}{2}}$. Figures 4 and 5 show the distributions observed for Kr ions and neutral atoms in Kr, and for Xe ions and neutral atoms in Xe. These are very similar to the Ar in Ar results previously reported. At low E_0, the ion produces a relatively greater characteristic yield with the difference between the ion and the neutral atom projectile becoming less for higher collision energies. Since the ion beam will contain a neutral atom component which is appreciable in this case of resonant charge exchange in the ionization region, one might expect some like groups in the ion and neutral atom cases but with these less prominent in the case of the ion. Approximately 25% of the ion beam is believed to be neutralized on reaching the region of the ionization chamber in which the observed electrons originate.[1] This similarity is particularly evident in $Kr^{+,0}$–Kr. Quite apparent for the ion and to a lesser extent for the neutral atom projectile is the increased emphasis on the higher excitation energies with increasing collision energy. The Kr^+–Kr spectra like Ar^+–Ar seem to have three groups so close that separation is not possible with the present analyzing system. The energy range associated with these groups varies in the way expected from the energy-level structure in the rare gases, 7–10 eV for Xe^+–Xe, 8–13 eV for Kr^+–Kr, and 10–14 eV for Ar^+–Ar at 3.0 keV. These are in general agreement with the results of Moe and Petsch[8] for the ionization of the rare gases by K ions.

SUMMARY

The ionization resulting from collisions of atoms and ions of several keV energy produces groups of electrons of definite energy as well as electrons with a broad energy spectrum. The origin of the characteristic electrons seems to be a process of autoionization of one of the particles involved. That relatively few states subject to autoionization are excited in the collision would seem to indicate rather limited selection rules for the process. The results here indicate that measurements of sufficiently high resolution and accuracy should yield information on the decay rate of the autoionized states and on the Stark displacement in high fields.

ACKNOWLEDGMENT

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[7] T. Wu, Phys. Rev. **66**, 291 (1944).

[8] D. Moe and E. Petsch, Phys. Rev. **110**, 1358 (1958).